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Hypochlorite as a Third Stage in the Bleaching of Neutral Sulfite Semichemical Aspen

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HYPOCHLORITE AS A THIRD STAGE IN THE BLEACHING OF NEUTRAL SULFITE SEMICHEMICAL ASPEN

A thesis submitted by

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GLOSSARY

D.P.—Degree of polymerization.

5% KOH Hemi--Hemicelluloses extracted from pulp by 5% potassium hydroxide.

16% KOH Hemi--Residue from 5% KOH hemicellulose preparation re-extracted with 16% potassium hydroxide.

A.R.C.--Alkali-resistant cellulose-that residue remaining after the 16% KOH hemicellulose determination.

cuen—Cupriethylenediamine.

0, 1.5, 3, 6,--Designations for pulps, the numbers refer to the percentage of hypochlorite applied in the third stage (based on the pulp charged to the stage). Standard conditions for the stage are: Two hours bleaching time, pH 10-10.5, and temperature 40 $\pm$ 1°C.

9-2-2-Chromatographic developer composed of ethyl acetate: acetic acid: water in a volume ratio of 9:2:2. System separates both sugars and acids.

10-3-3-Chromatographic developer composed of butanol: pyridine: water in a volume ratio of 10:3:3. System separates sugars but not acids.

INTRODUCTION

The neutral sulfite semichemical (NSSC) process was developed in the early twenties, but did not find immediate commercial application. The necessity for increased utilization of hardwood stands by the paper industry has focused attention on the process as it is eminently suited to the high yield pulping of these woods to produce an easy beating pulp of very high hemicellulose content suitable for a wide range of products.

Early investigations in NSSC pulping and bleaching were entirely practical; the types of woods which could be processed, the range of operating conditions required, and other information necessary to the successful application of the process received attention. Recently, attention has been directed toward the more fundamental aspects of the process. A comprehensive study of the NSSC processing of aspenwood has been the subject of three Institute theses which covered pulping and the first two stages of bleaching. In the sequence, Lea (1) investigated the removal of hemicellulosic components from the wood by NSSC cooking liquors. This work was amplified by Quick (2), who investigated the rate and order of removal of the hemicelluloses, and the effects of the chlorination and extraction stages were detailed by Boehm (3). Some work done in Sweden on birch and spruce NSSC pulps confirms the results obtained in the first two bleaching stages and indicates a few of the effects of the hypochlorite stage (4). The work to date leaves the hypochlorite stage as the obvious next step in the investigation of NSSC pulps, and was an indirect factor in the choice of this thesis.

Bleaching, in a general sense, is the whitening brought about by the removal of colored components or the destruction of chromophoric groups. The chlorination and extraction stages may be considered as part of the cooking in this sense as the pulp leaves the extraction stage at a lower brightness than it had originally, but has a very much lower lignin content. Boehm (3) concluded that chlorination removed 9.5% lignin and the caustic-extraction stage an additional 4.2%, while both stages removed a total of only 0.9% carbohydrate material (expressed in terms of unbleached pulp) which was hemicellulosic in nature. Oxidative bleaching, such as produced by hypochlorite, is possible only because the attack of the oxidizing agent on the colored groups is much more rapid than its attack on the cellulose fraction of the fiber.

The practical aspects of hypochlorite bleaching of NSSC pulp have received a great deal of attention in the literature, and a large body of empirical data has been accumulated (5-9). The process can be carried out as a single stage or as the final stage of a multi-stage bleach. Comparisons between single stage and multi-stage bleaching have been made (6, 7). In general, the high lignin content of the unbleached NSSC pulps makes it difficult to obtain good brightnesses in one stage; the maximum brightness obtained in single-stage bleaching is between 70-75 while values above 80 can be obtained by multi-stage bleaching. Bleaching improves the strength properties of the NSSC pulps by removing lignin, and even a single stage bleach produces appreciable strength increases. It is difficult to ascertain the amount of improvement in multi-stage bleaching due to the hypo-

chlorite stage itself, as only scanty data--given at various freeness values--are available (9). If NSSC pulps behave like the usual chemical pulps in the hypochlorite stage, a decrease in strength would be expected. The present investigation will clarify this point.

Recent works on the hypochlorite oxidation of sulfite and sulfate pulps, when the hypochlorite is used as the last stage of a bleaching sequence, show the same general trends as observed for the bleaching of cotton. This is to be expected, since these pulps are approaching pure cellulose in composition. Small amounts of lignin, hemicelluloses, and extractives alter reaction rates, but the prolonged bleaching times employed by all of these investigators make the degradation of cellulose the dominant factor in the studies. The experimental work of these investigators may be summarized as follows:

(1) pH is extremely important in controlling both the rate and the course of the bleaching reactions. Low pH values favor the formation of reducing groups, low pulp viscosity, high alkali solubility, high β and low α-cellulose values, and high yellowing (reversion) values. High pH conditions reverse these trends, giving pulps high in acidic and low in reducing groups. The reaction rate (as far as degradation of cellulose is concerned) goes through a maximum in the neutral pH range (10-13).

(2) As the pH increases to 10, the reaction rate decreases, and formation of carboxyl groups reaches a maximum, reducing groups a minimum. Increasing the pH to 12 decreases the reaction rate further, but at the same viscosity the carboxyl content of pulps bleached at pH 10 and 12 is identical (13).

(3) The brightness of the bleached pulp increases as the pH of the bleaching stage is increased from pH 2 to pH 10 if all other variables are fixed; further pH increases produce a slight decline in brightness under these conditions (14).

(4) There is no parallel between the oxidation potential and any of the bleached pulp properties as functions of pH. This is taken as an indication that specific reaction mechanisms are more important in bleaching than the oxidation potential of a given system (14, 15).

(5) Temperature has no effect on the course of the reactions, (at least to 60°C.), but the reaction rate doubles for every 7°C. rise in temperature (10).

(6) Hypochlorite bleaching appears to follow second order reaction kinetics (16).

No equivalent investigations have been made for NSSC pulps. Bjorqvist, et al., (4) found that pentosans and uronic acids are resistant to bleaching in the range pH 8.5-10.0, lignin removal goes to practical completion, and a small amount of noncellulosic hexosans are lost in this stage. No studies of the degradation or the possible degradation of the cellulosic and hemicellulosic components of the pulp was carried out, which might have been an important consideration in determining the physical properties of the bleached pulps.

NSSC aspen pulp is quite different from the softwood chemical pulps that have been the subjects of previous bleaching investigations,

possessing appreciably greater amounts of carboxyl groups and hemicelluloses. The lignin also differs from that of the chemical pulps not only chemically but also from the standpoint of distribution, as NSSC pulps have more shives or fiber bundles than bleaching grades of chemical pulps, and thus a great deal of middle lamella lignin is present in the pulp. The importance of the distribution of major components through the fiber walls has been indicated by Jayme and von Koppen (17), for sulfite and sulfate pulps. It is possible that hypochlorite bleaching will have some effect on this distribution in NSSC pulps with concomitant changes in physical properties, a point that has not yet been elucidated in the literature.

The effect of pH on hypochlorite bleach liquor has been studied by many investigators. It has a marked effect on liquor composition which probably exerts a decisive influence on the course of the bleaching reactions. In the pH range of immediate interest, the liquor is a mixture of hypochlorous acid and hypochlorite ion(neglecting hydrogen and chloride ions which are not bleaching agents); above pH 10, the system is practically 100% hypochlorite ion. In spite of this fact, no one has positively identified the actual "bleaching agent" in the system. The action of hypochlorite on individual pulp components will be considered to clarify some of the effects noted in pulp bleaching.

Further difficulties appear when characterization of the oxidized pulps is attempted. Without considering the complications introduced by the presence of lignin and hemicelluloses, the properties of the oxidized cellulose are markedly affected by the pH of oxidation,

presumably because the composition of the oxidizing system is dependent on pH. Hypochlorite is a non-specific oxidant, capable of oxidizing any hydroxyl or carbonyl group in the cellulose molecule to carboxyl in contrast with the more specific attack of periodate on position 2 and 3, or nitrogen dioxide on position 6 hydroxyls. In acid media, the hypochlorite system produces a "reducing" oxycellulose containing predominantly carbonyl groups. Alkaline conditions yield a product high in carboxyl. The earliest work that gave a comprehensive picture of the effect of hypochlorite on cellulose as a function of pH is the classic work on the bleaching of cotton of Britwell, Clibbens, and Ridge (18). They found the rate of reaction between hypochlorite and cotton was very slow, but did go through a maximum at the neutral pH range.

Fundamental studies have done much to clarify the behavior of the oxidized celluloses. The reducing type oxycelluloses show alkali instability and the acidic type do not. The most probable explanation for this behavior is the result of investigations carried out on β ethers and their behavior on alkaline oxidation. Helfrich (19) demonstrated that the presence of an electronegative group β to an ether link confers alkali sensitivity to that link; thus, such groups would confer alkali sensitivity to the 1-4 oxygen link or the ring oxygen of the cellulose molecule. The carboxyl group does not participate in this mechanism even though it is electronegative, as ionization greatly reduces its electronegative character. It is interesting to note that three out of the four possible scissions in the cellulose chain made possible by the introduction of electronegative groups pro-

duced by random oxidation occur at the 1-4 link (20). Kaverzneva (21) has shown that other groups besides aldehyde and carboxyl are produced by cellulose oxidation. Keto groups, lactones, and esters have been identified. Some of these groups are stable only in certain pH ranges--another reason for the observed variations in oxidized cellulose composition with pH.

The oxidation of lignin by hypochlorite has received considerable attention, but the complete picture of the reactions that occur is not yet clear (22, 23). The reactions are rapid and severe; the lignin molecule is extensively degraded to soluble products, and its removal from pulp is quantitative for practical purposes. Experimental evidence indicates that the first 6 or 7 moles of hypochlorite per lignin building unit act by chlorination and further reaction destroys the characteristic absorption peak at 280 mmu., interpreted as an oxidative destruction of aromatic rings. Some demethoxylation also occurs. Richtzenhain (23) has shown that the ortho or para position from a phenolic hydroxyl cannot be blocked if the oxidation is to proceed at a rapid rate. A possible mechanism for the general course of the reaction is presented by White, et al., (22).

No comparable investigations have been made on the hemicelluloses. Whistler (24), studying the mechanism of polysaccharide oxidation, showed that the xylan isolated from corn cobs was resistant to oxidation.

In summary, it might be said that our knowledge of bleaching reactions is still fragmentary, so it is impossible to make accurate

predictions of the effect of hypochlorite on NSSC pulps. There were several interesting problems that received clarification in this investigation: For example, the effect of lignin removal on pulp properties at low (ca. 1.0%) lignin contents, and the fate of the hemicellulose fraction, with particular emphasis on D.P. changes. Fundamental changes in fiber properties that can explain the observed effects, were discovered in the course of the investigation and provide insight into NSSC bleaching that may lead to more intelligent process control, and contributes to our knowledge of bleaching in general.

The experimental data obtained in the investigation of hypochlorite as the third stage for a fully bleached NSSC aspen pulp are presented and discussed in the next section of this report.

EXPERIMENTAL RESULTS

SUMMARY OF EXPERIMENTAL CONDITIONS

An "easy bleaching" NSSC aspen pulp was prepared for these bleaching studies. As the primary concern of the thesis is the effects of the hypochlorite stage itself, data pertaining to pulp preparation, cooking, and the first two stages of bleaching are presented in the "Appendix" of this report. However, to establish a background for the interpretation of the experimental results, a summary of important conditions is presented at this time.

The NSSC pulp was cooked to a chlorine demand of 13.2% (unbleached pulp basis). Of this, 12% was applied as gaseous chlorine in the chlorination stage and the remainder applied as hypochlorite in the last stage. Caustic extraction was done with 2% sodium hydroxide (unbleached pulp basis). The yield on this basis was 80.5%, which compares reasonably well with the 82% reported by Boehm (3) who used the same wood but different chlorination conditions. Two commercial pulps that had been chlorinated and extracted were analyzed for lignin and compared with the lignin content of the experimental one. The data are presented in Table I, and show that on this basis at least, the pulps are similar.

TABLE I

LIGNIN AFTER CHLORINATION AND EXTRACTION[1]

Pulp	Klason Lignin, %	Soluble Lignin, %
Commercial 1	0.65	0.53
Commercial 2	1.05	0.64
Boehm's pulp (3)	2.4	1.9
Experimental pulp, this work	1.22	0.39

[1]g. lignin/100 g. pulp (moisture and extractive-free basis)

The hypochlorite stage conditions were chosen to permit the evaluation of the effect produced by commercial bleaching. As the changes in pulp properties are quite small in this range, it was necessary to select a series of increasingly severe bleaching conditions to permit determination of the magnitude and direction of these changes.

The "normal" bleaching conditions are: 1.5% available chlorine (on the basis of pulp charged to the stage), bleaching carried out at 10% consistency at 40 ± 1°C. for 2 hours at pH 10.0-10.5. This produced a pulp of 79 G. E. brightness, but only slight changes in chemical properties were detactable. To create measurable changes in chemical properties, all conditions except the hypochlorite concentration were held constant and further experiments made. The brightness and chlorine consumption data are presented in Table II.

TABLE II

HYPOCHLORITE BLEACHING

Available Chlorine, %	Residual Available Chlorine, % of applied	Bleaching Time, min.	G.E. Brightness, %
1.5	71	12	68.6
1.5	60	30	71.0
1.5	47	60	74.3
1.5	20	120	79.0
3.0	26	120	85.0
6.0	47	120	85.7

The pulps apparently behave in a perfectly normal fashion as far as chlorine consumption and brightness increase with bleaching time are concerned. It is interesting to note the "ceiling" on brightness that can be obtained with hypochlorite in this stage. Doubling the hypochlorite concentration from 3 to 6% yielded only an additional 0.7 pt. brightness, while at the lower level of hypochlorite, the same twofold increase gave a 6.0 pt. gain. These pulps were evaluated for changes in physical and chemical properties. All tests were referred to the pulp from the caustic-extraction stage (0 hypochlorite) to determine the extent of the effects. The pulps are designated by numbers, indicating the amount of hypochlorite used in the third stage. Unless special mention is made, bleaching time was 2 hours.

PULP CHEMICAL PROPERTIES

The results of chemical characterization of the caustic-extracted and hypochlorite-bleached pulps are presented in Table III. The most striking feature of the data is that even at high hypochlorite concen-

TABLE III

PULP CHARACTERIZATION

Hypochlorite applied in third stage, %	0	1.5	3.0	6.0
Bleached yield, %		99.	99.	98.
G.E. Brightness, %	68.0	79.0	85.0	85.7
Lignin[1]				
Klason lignin, %	1.22	0.68	0.27	0.13
Soluble lignin[2], %	0.39	0.29	0.16	0.12
Sum of above	1.61	0.97	0.43	0.25
Phosphoric acid[3] lignin, %	1.01	0.74	0.57	0.49
Carbohydrates[4]				
A.R.C., %	74.2	74.0	74.4	74.6
5% KOH hemis, %	14.1	-	-	14.0
16% KOH hemis, %	10.1	-	-	10.6
Extractives[1]				
95% Ethanol extract., %	0.63	-	-	0.84
Carboxyl, meq./100 g.				
Pulp	16.3	15.7	15.1	15.0
A.R.C.	3.1	3.5	4.3	4.1
Sulfur[4], %	0.13	0.083	0.071	0.057
Viscosity data				
Pulp D.P.[5]	1960	1680	1500	1330
A.R.C. D.P.[5]	1850	1610	1560	1460
5% KOH Hemi D.P.[6]	139	139	139	139
16% KOH Hemi D.P.[6]	150	-	-	146

1 Ovendry, extractive-free pulp basis
2 Measured at 230 mμ
3 Measured at 280 mμ
4 Ovendry pulp basis
5 $[\eta]$ calculated from Martin equation. D.P. calculated from equation $170\,[\eta]=D.P.$
6 Calculated from $D.P.=[\eta]/4.4\ (10^{-3})$

trations, the reaction is primarily with lignin; it is the only substance removed in appreciable quantity. Hypochlorite degrades cellulose, as shown by viscosity measurements, but under the experimental conditions does not affect the amount of alkali-resistant cellulose. Hemicelluloses are even more resistant to the action of hypochlorite than cellulose; no degradation occurs. It has been previously established that in this pH range, the quantity of hemicellulose (measured as pentosan) is not affected by low concentrations of hypochlorite (11, 12), but this could have been the case even if some degradation occurred. The amount of hemicellulose extracted from the pulp by successive treatment with 5 and 16% potassium hydroxide according to Wise and co-workers (25) is unaffected by bleaching.

A rough material balance shows that removal of lignin is the most significant factor in controlling bleached yield. This is presented in Table IV.

TABLE IV

MATERIAL BALANCE[1]

	Hypochlorite, %	0	1.5	3.0	6.0
(1)	Lignin present after bleaching, %	1.61	0.97	0.43	0.25
(2)	Lignin removed by bleaching, %	-	0.64	1.18	1.46
(3)	Bleached pulp yield, %	-	99.0	99.0	98.0
	Sum of (2) and (3), %	-	99.6	100.2	99.5

[1]Basis: 100 g. extracted pulp

Results expressed on extractive-free basis

Lignin represents sum of soluble and Klason lignin

The amount of material extracted with hot 95% ethanol from the pulp is not significantly changed by bleaching, but the extractives are whitened by the action of the hypochlorite.

LIGNIN DETERMINATION

There is some difficulty in obtaining a meaningful lignin determination on bleached pulps. Lignin has been altered chemically by sulfonation, oxidation, demethoxylation, and other reactions by processing, and is present in such small amount that interference in the lignin determination caused by carbohydrate degradation products may be significant. In the case of NSSC pulps, Klason lignin measures something rather specific from the standpoint of physical structure, and of great interest from the standpoint of a pulp's physical properties--it correlates with pulp behavior in certain respects and so is a useful

test, even at low levels--a point which will be further developed in the section on microscopic studies. Soluble lignin is determined as that material in the filtrate from the Klason lignin determination which absorbs light at 280 and 230 mμ. Boehm (3) has demonstrated that it may be in error from several causes: carbohydrate dehydration products tend to make the result high, compound formation between insoluble lignin and carbohydrate-dehydration products tend to make the result low. The amount of soluble lignin was calculated using the absorption coefficient determined for aspenwood native lignin in dioxane (26). It is possible that the bleaching stage could have altered the absorption coefficient of the lignin so it no longer is the same as the assumed value, which would introduce an error of unknown magnitude into the determination. Recourse to the determination of soluble lignin by the phosphoric acid method (27) is of no help. Comparison of the results for soluble lignin determined on the Klason lignin filtrate and the phosphoric acid method reveals a nearly constant bias of 0.4% between the methods in all except to O pulp sample. Results are high with the phosphoric acid method probably due to the formation of furfural, hydroxymethyl furfural and other carbohydrate dehydration products; the amount is practically constant because the reaction time is constant. The anomalous results obtained for the O sample are probably due to the fact that all the lignin did not go into solution in the phosphoric acid.

By calculating the soluble lignin from the optical density of the filtrate at 230 instead of 280 mμ, interference from carbohydrates is reduced (3), it has also been demonstrated by Boehm (3) that something of noncarbohydrate nature is being measured, and it seems reasonable to

account for this material by reporting "soluble lignin." It is realized that the quantity may be in appreciable error, but it is not a large factor in the material balance and may be valuable for comparative purposes.

CARBOXYL DETERMINATION

A small but significant change (determined by Student's "t" test on the original data) occurs in the "carboxyl" content of the pulp as bleaching proceeds. "Carboxyl" content was measured by the method of Wilson (28) in which the pulp is treated with acid to convert all of the carboxyl groups to the acid form, washing out the excess acid with distilled water, and then adding the pulp to a measured volume of sodium bicarbonate solution. The change in titer of the bicarbonate solution is proportional to the amount of carboxyl groups present. This is only the case if lignin exhibits no ion-exchange capacity as the method actually is determining the over-all ion-exchange capacity of the pulp which is the sum of the contributions of cellulose, hemicellulose, and lignin. It is difficult to make accurate comparisons unless pulps have the same sulfonic acid content, but an idea of the magnitude of the ion-exchange effect contributed by the pulp components can be gained from the literature. At the same lignin content, a sulfate pulp contains 1.2% and a sulfite 2% uronic anhydride, while a NSSC pulp bleached to a lower lignin content contains about 4% uronic anhydride (17). The lignin in a sulfite pulp has a very high ion-exchange capacity due to the presence of sulfonic acid groups. It also contains groups that are not effective until the pH is neutral or slightly basic, behaving like hydroxy acids and phenols in this

respect. Sulfate pulp, of course, contains no sulfonic acid groups and contains less of the other groups as well. The exact nature of the lignin in a NSSC pulp has not been established, but it is known to contain sulfonic acid groups; other groups capable of exchange reactions are probably present as well.

Bleaching investigations on pulp with relatively low uronic anhydride content such as sulfite and sulfate (11-13) show an increase in the ion-exchange value due to the degradation of cellulose chains and the formation of carboxyl groups at the points of cleavage. Under bleaching conditions comparable to those employed for the normal bleach in this work, these pulps show a rise of 1.6-2.1 meq./100 g. in carboxyl content, while the NSSC pulp showed a 0.6 meq./100 g. decrease. An attempt was made to isolate the contributions of the pulp fractions to the over-all ion-exchange value to explain this apparently odd result. Carboxyl content of the isolated A.R.C. fraction (predominantly cellulose) increased about 1.0 meq./100 g. on bleaching with 6% hypochlorite. This measurement should be one of carboxyl content as this is the only exchangeable group that should be present in the A.R.C. The trend of these results is in the expected direction.

Lignin could contribute to the over-all ion-exchange value by virtue of its sulfonic acid groups and any other exchangeable groups it might possess. It is difficult to measure all of the exchange capacity associated with the lignin, but sulfur determinations were made and the exchange capacity calculated as if every sulfur-containing

group had a replaceable hydrogen atom. The pulp ion-exchange value was corrected for the contribution of lignin, on the stated assumption, and the A.R.C. contribution. The remainder was constant within experimental error and represents the contribution of the hemicellulose fraction which contains most of the uronic acids in the pulp. This is consistent with the inert behavior displayed by this fraction to hypochlorite and indicated in the chemical characterization of the pulp. The results are presented in Table V.

TABLE V

SULFUR CONTENT AND ION-EXCHANGE

Hypochlorite, %	0	1.5	3.0	6.0
Sulfur[1], %	0.13	0.083	0.071	0.057
Sulfur, meq./100 g. pulp	4.1	2.6	2.2	1.8
Over-all exchange value[2]	16.3	15.7	15.1	15.8
Lignin exchange value	4.1	2.6	2.2	1.8
A.R.C. exchange value	3.1	3.5	4.3	4.1
Hemicellulose exch. value[3]	9.1	9.6	8.6	9.1
100 S/lignin	8.07	8.56	16.5	22.8

[1]Ovendry pulp basis

[2]Exchange value expressed in meq./100 g. pulp, ovendry basis

[3]Calculated by subtracting the sum of lignin and A.R.C. exchange values from the total value for the pulp.

An interesting effect is the increase of the sulfur/lignin ratio on bleaching. This is unexpected, but might be the case if the sulfur groups are located in the lignin least accessible to the action of hypochlorite. This would be in the "shives" or fiber bundles present in the pulp which are resistant to hypochlorite because they have a massive concentration of lignin. Staining reactions support the concept,

but are open to other interpretations as the total amount of lignin is also a variable affecting the intensity of the staining.

DEGREE OF POLYMERIZATION OF PULP

The next important consideration in hypochlorite bleaching of NSSC pulps is the degradation of the cellulose and hemicellulose fractions, which play important roles in sheet strength and other physical properties. The viscosities of the pulp and A.R.C. fractions were determined at constant concentration and intrinsic viscosities calculated from the Martin equation (29); D.P. values were obtained by multiplying the intrinsic viscosity values by a constant (see p. 93). These fractions had very high D.P.'s, therefore the influence of variable shear rate on the intrinsic viscosity measurements was appreciable and could have led to errors in the calculated D.P. values. The procedure outlined minimizes the effects of variable shear rates making it possible to follow accurately the D.P. changes produced by bleaching with a simple technique. The D.P. of the A.R.C. fraction parallels that of the pulp, except that it finally is at slightly higher values; this is expected since the contribution of the short chain hemicelluloses is not present in this fraction.

DEGREE OF POLYMERIZATION OF HEMICELLULOSE

At low D.P. values, the effect of shear is negligible, permitting the intrinsic viscosity to be obtained by extrapolation of vicosities measured at different concentrations. This procedure was used to obtain hemicellulose intrinsic viscosity and, indirectly,

D.P. The results of the viscosity measurements are presented in Figure 1. No significant degradation is noted in the analytically defined hemicellulose fractions of the pulp. A 2.7% decrease in D.P. is noted in comparing the 16% hemicellulose fractions prepared from the 0 and 6 pulp, but this is probably within experimental error. It is of interest to compare these D.P. results with those obtained by other investigators on the same wood, but at different stages of processing. The results are presented in Table VI.

TABLE VI

ASPEN HEMICELLULOSE D.P.
(P. tremuloides)

Treatment	Extraction of Hemicellulose	D.P.	Reference
Aspenwood	Combined 5 and 16% KOH	100-120	Lea (1)
NSSC pulp	5% KOH, 16% KOH	210-230, 184-210	Quick (2)
NSSC pulp after:			
Chlorination and extraction	5% KOH	139	
	16% KOH	150 (0 pulp)	
Hypochlorite	5% KOH	139	
	16% KOH	146 (6 pulp)	

The hemicellulose D.P. after bleaching is nearly the same as that of the hemicelluloses in the original wood. Cooking apparently increases the D.P. by the removal of some low molecular weight material, and either the chlorination or extraction stage may produce some degrading. The evidence is not conclusive at this point as Quick used a different cooking liquor which might affect the results.

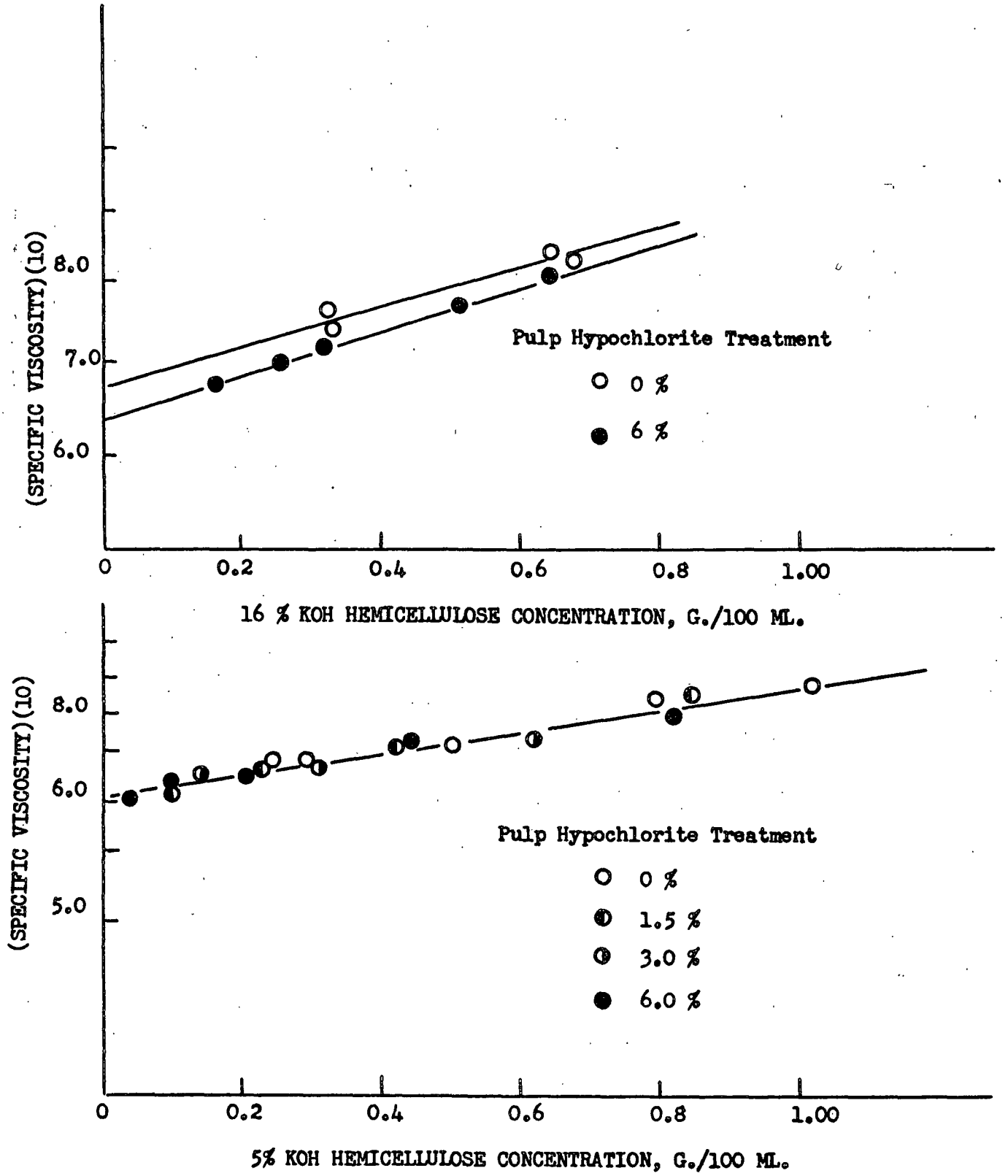

Figure 1. Intrinsic Viscosity Determinations For Extracted Hemicellulose Fractions

PHYSICAL PROPERTIES

EFFECT OF HYPOCHLORITE ON HANDSHEET PROPERTIES

Sheet Strength: The effect of bleaching on the physical properties of NSSC pulps is of primary interest to the papermaker. Studies of the physical properties of handsheets prepared from the pulps were carried out to establish the direction and magnitude of these changes. The series I (solvent-dried)[1] pulps were refined in a Jokro Mill and handsheets prepared at the 5, 10, 20, and 25-minute beating intervals. After conditioning, the physical properties of the sheets were measured. Correlation of sheet strength with freeness yielded ambigous results as freeness is affected by too many variables that do not affect sheet properties to the same extent that they affect the freeness test. A striking dependence was noted when sheet specific gravity was plotted against beating time. The pulps arranged themselves in order--higher values of sheet density being reached at the same beating time as bleaching became more severe. This relationship is presented in Figure 2.

Apparently the differences in handsheet properties between solvent dried and "never dried" pulps is negligible. It was feared that residual bonding might have some deleterious effect on physical properties, but sheets prepared from 1.5 bleached pulp that had never been dried were compared with those prepared from the same pulp that had been solvent dried from methanol, and no significant differences in sheet density or burst were noted.

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[1]Solvent drying refers to the displacement of water from a pulp slurry with alcohol and subsequent removal of the alcohol by air drying. The procedure greatly decreases "hornification" of the pulp. (see p. 88).

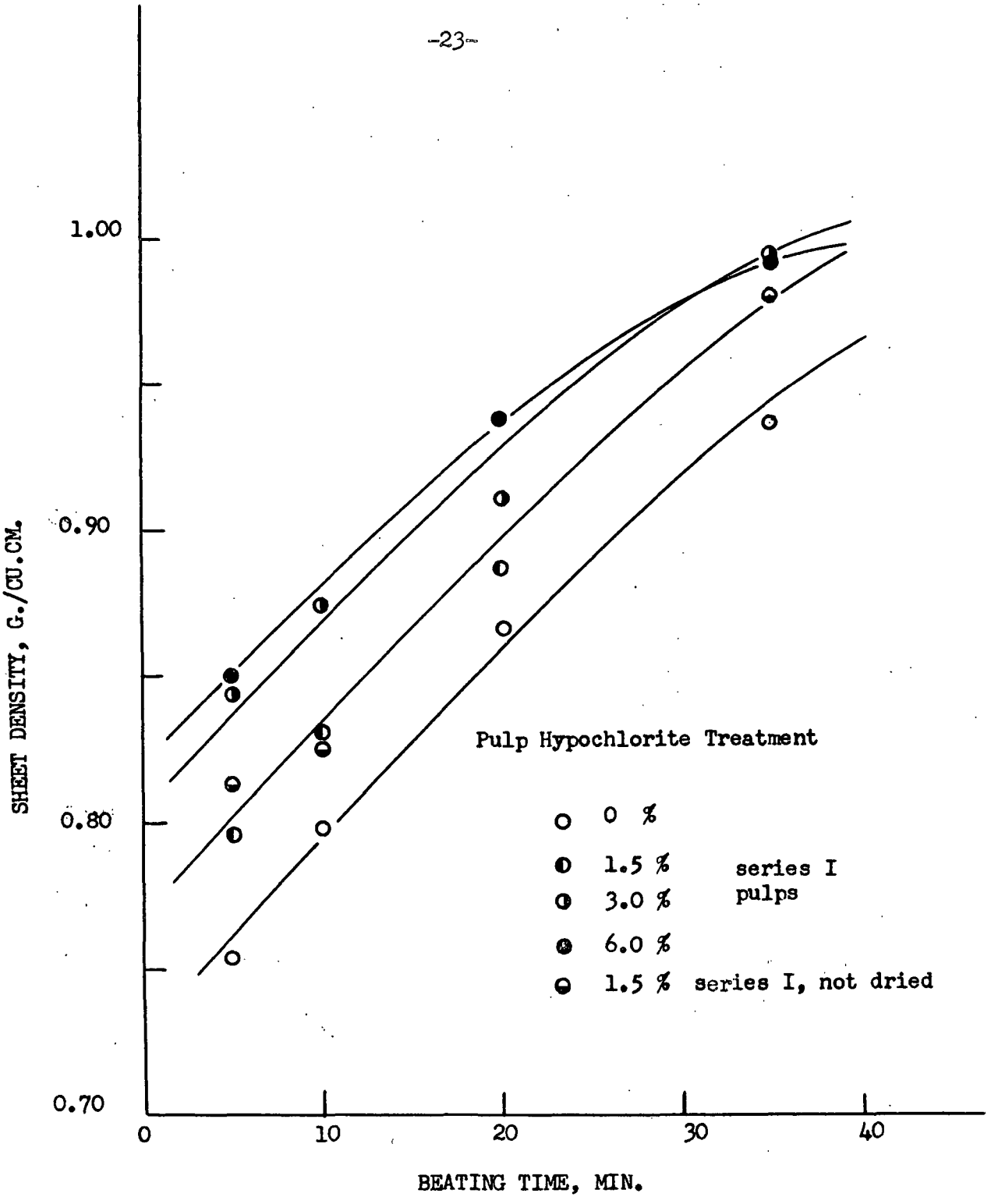


Figure 2. Development of Sheet Density of Bleached Pulps on Milling in the Jokro Mill

As sheet density appeared to be such an important parameter, tensile strength--expressed as breaking length--and burst were plotted as functions of sheet density. Figures 3 and 4 give the results. It is obvious from inspection of the graphs that all sheets have the same strength at the same sheet density. It would appear that the hypochlorite promoted fiber—fiber bonding without seriously affecting fiber strength. This may be the net result of at least two opposite effects that occur simultaneously. One is the weakening of the fibers produced by the oxidative attack of the hypochlorite, and the other, the increased ability of the pulps to produce fiber-fiber bonds brought about by bleaching. As long as the formation of the fiber-fiber bonds balance or exceeds that necessary to balance the weakening effects of degradation the sheet strength will remain unaffected or be increased by bleaching. The data from which these results are derived are presented in Table VII.

To determine what physical changes were produced in the individual fibers by hypochlorite that might explain these observed effects, fiber specific surface, effective specific volume and compressibility were determined by the filtration resistance technique of Ingmanson (30) on series II (never dried) pulps. It was necessary to prepare the series II pulps for these determinations as variations in washing, centrifuging, and solvent drying affected the amount of fines and ease of dispersion of the series I pulps. These variations were too small to affect sheet tensile strength but did affect filtration resistance. Series II pulps were bleached under conditions identical to series I, but were carefully dewatered on a suction funnel to 15% consistency and not washed to eliminate the loss of fines. By giving the bleached pulps identical histories, satisfactory measurements were obtained.

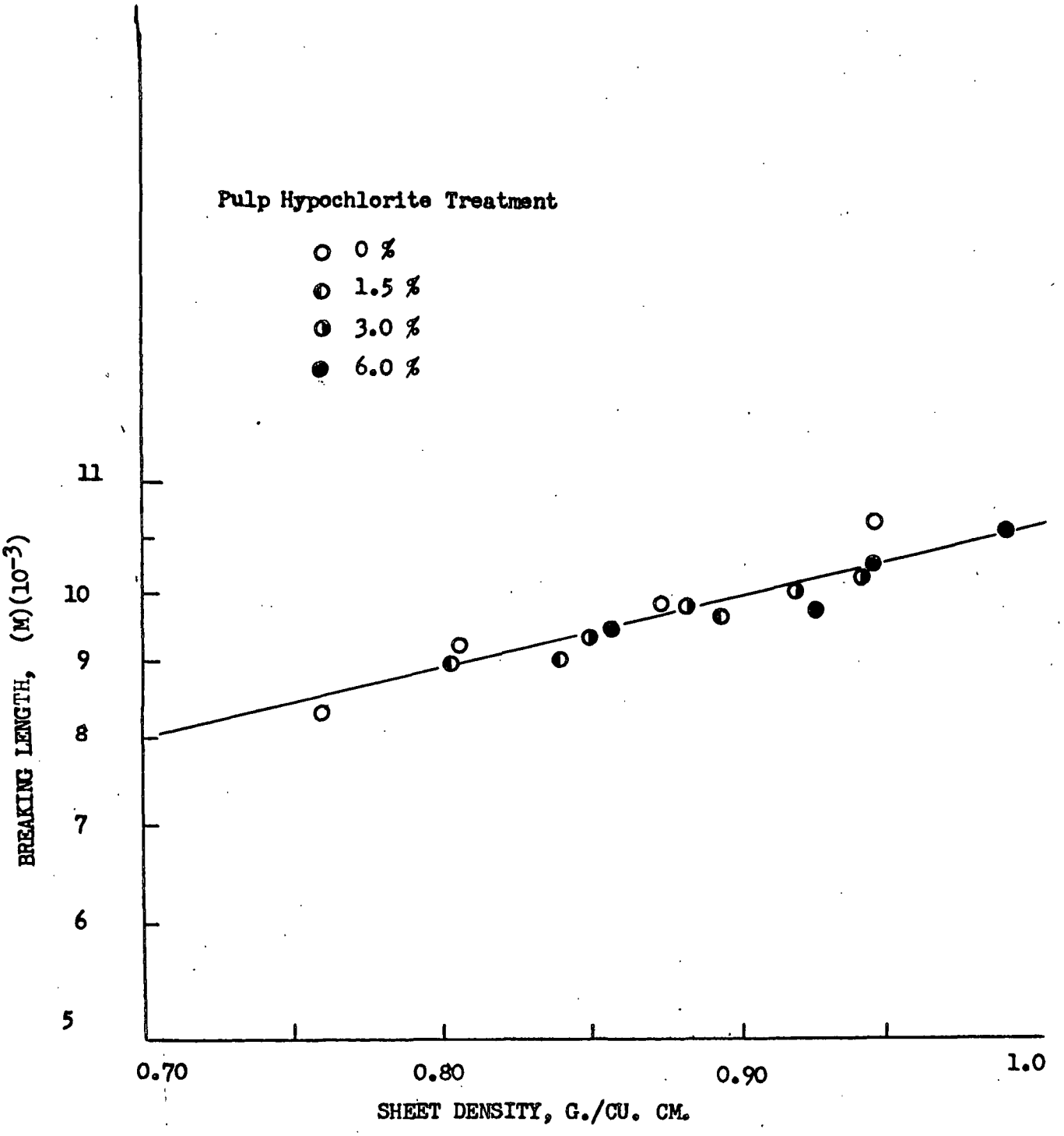


Figure 3. Relationship Between Breaking Length of Beaten, Bleached Pulps and Sheet Density

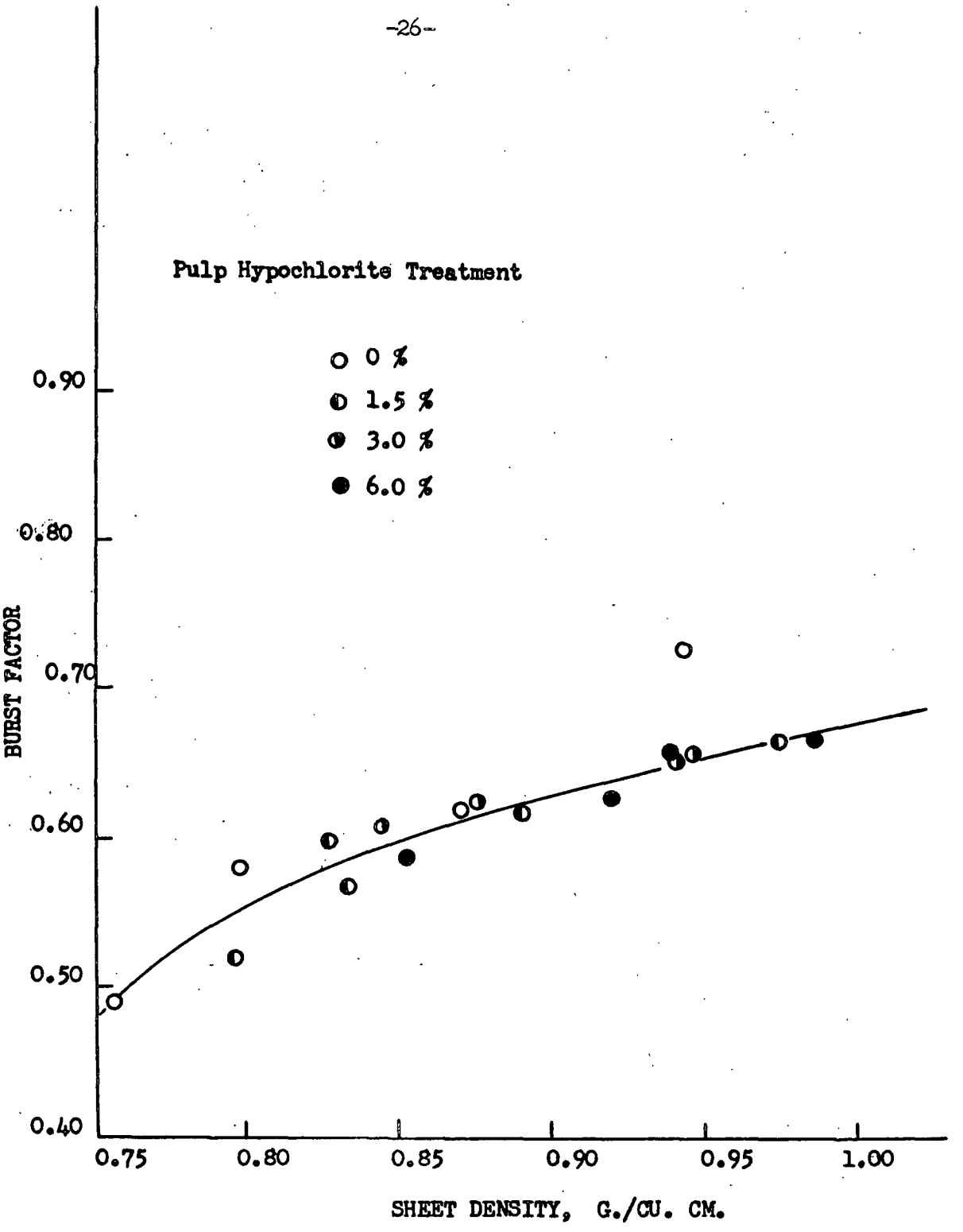


Figure 4. Relationship Between Burst Factor of Beaten, Bleached Pulps and Sheet Density

TABLE VII

PULP PHYSICAL PROPERTIES

Series I Pulps

Milling time, min.		5	10	20	35
Sheet density, g./cu. cm.	0[1]	0.754	0.799	0.867	0.937
	1.5	0.796	0.831	0.887	0.971
	3.0	0.844	0.875	0.911	0.985
	6.0	0.850	0.916	0.938	0.983
Burst factor, g./sq. cm./g./sq.m.					
	0	0.49	0.58	0.62	0.73
	1.5	0.52	0.57	0.62	0.69
	3.0	0.61	0.63	0.66	0.65
	6.0	0.59	0.63	0.66	0.67
Tappi opacity					
	0	64.7	57.1	48.6	48.0
	1.5	59.1	53.7	47.7	40.9
	3.0	60.2	60.0	51.0	43.4
	6.0	59.2	53.7	44.9	40.0
Breaking length, m.					
	0	8290	9170	9730	11020
	1.5	8940	8940	9580	9450
	3.0	9210	9700	9920	10270
	6.0	9380	9660	10390	11090
S.-R. Freeness					
	0	669	608	480	315
	1.5	672	621	487	192
	3.0	670	604	465	291
	6.0	651	587	442	288

Series II Pulps

	Sheet Density, g./cu. cm.	Specific Surface Area, cm. sq./g.	Effective Specific Vol., cu. cm./g.
0[1]	0.69	15,400	2.72
1.5	0.75	16,400	2.80
3.0	0.75	16,600	2.85
6.0	0.78	16,700	2.87

	Compressibility at 50 cm. Pressure	Burst Factor, g./sq.cm./g./sq.m.
0	0.104	0.316
1.5	0.115	0.376
3.0	0.115	0.383
6.0	0.115	0.389

[1]Percent hypochlorite applied to stage on basis of pulp charged to the stage

FILTRATION RESISTANCE AND DERIVED RESULTS

Filtration resistance and a separate compressibility determination were used to calculate the specific surface and effective specific volume. These fiber characteristics are related by theoretical considerations to the filtration resistance of the pulps, which is of itself interesting to the papermaker as it gives a relative picture of how the pulps will run on the paper machine. Average filtration resistance was plotted as a function of pressure drop with the amount of bleaching as a parameter of the family of curves in Figure 5. Qualitatively, the data indicate that appreciable changes in operating conditions on the machine would be necessary in changing from the 0 pulp to any of the bleached pulps, and that all of the bleached pulps should behave in about the same way.

The experimental values for effective specific volume, specific surface and compressibility are reported at the bottom of Table VII. These increase with increasing bleaching which has an important bearing on the physical properties of these pulps.

Effective specific volume is a measure of fiber swelling. Filtration resistance data do not yield an "actual" specific volume, such as might be calculated from microscopic measurements, but rather the hydrodynamic volume of the fiber—i.e., the volume of the fiber plus that of the envelope of water immobilized by the fiber through mechanical entrapment in capillaries and fibrils, or held by secondary valence forces. Objections can be raised to all of the available methods for measuring fiber swelling. As long as the method permits correct ranking of the pulps it is satisfactory for comparison purposes.

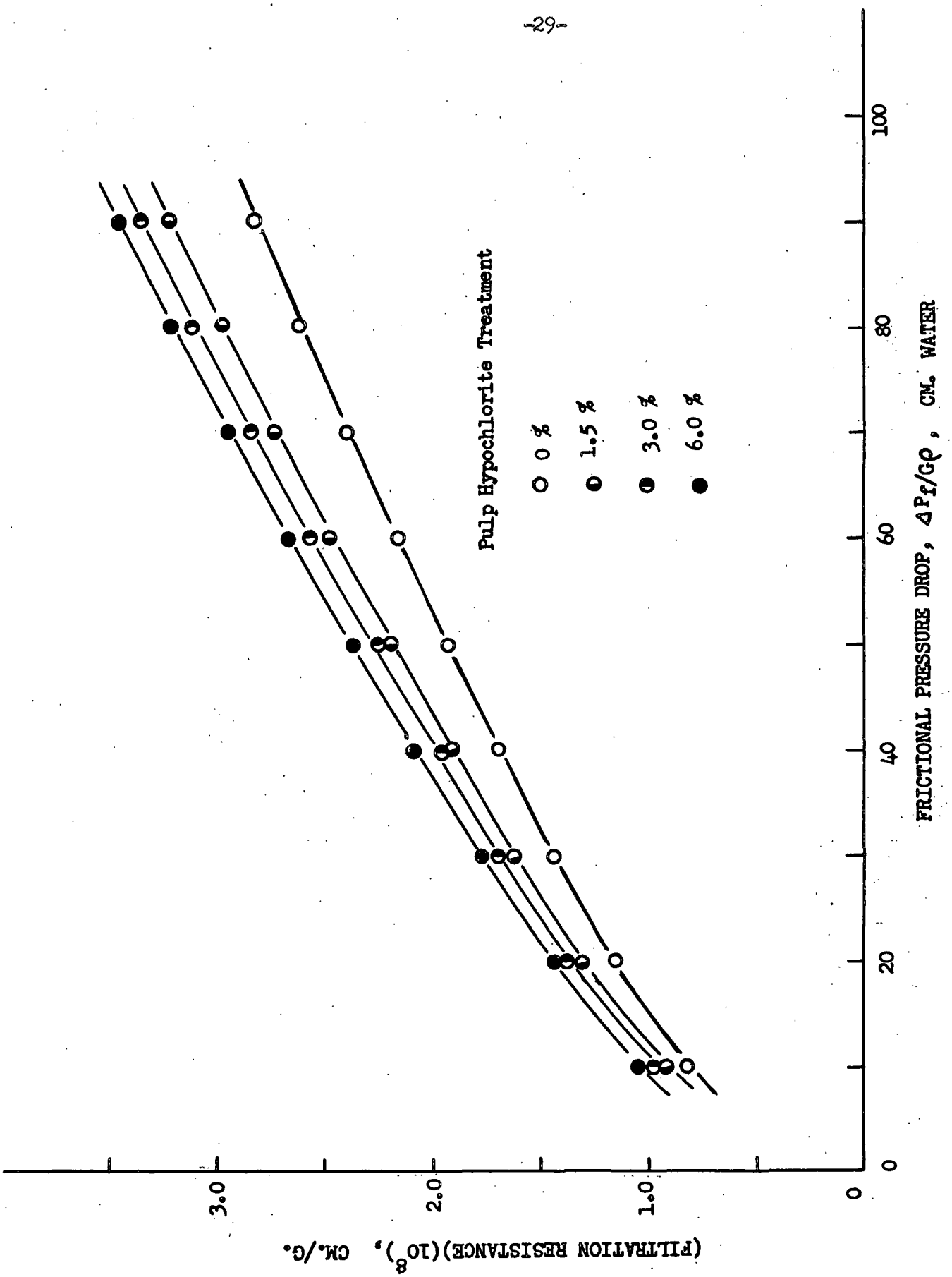


Figure 5. Filtration Resistance of Bleached Pulps

Ingmanson (30) has shown that filtration resistance techniques give the same relative ranking as air permeability measurements, so it seems reasonable that comparisons made between similar pulps will yield satisfactory results. Swelling power has been recognized as an extremely important pulp property. Gallay (31) has suggested that it is the primary factor in the interrelationship of pentosan content with ease of refining and sheet strength. Young and Rowland (32), using a dilatometric technique, investigated a variety of pulps and found a definite correlation between pentosan content and swelling power. Gallay (31) indicates that other factors have an effect in the case of sulfite and sulfate pulps as pulps with the same swelling power have different properties. This has been attributed to the difference in the distribution of lignin and hemicellulose in these pulps by Jayme and von Koppen (17).

EFFECT OF LIGNIN ON SPECIFIC VOLUME

In the present experiments, the hemicellulose content is substantially constant for all the pulps, only lignin changing. Plotting the effective specific volume as a function of the Klason lignin content shows that the swelling power of these NSSC pulps is a linear function of their lignin content (Figure 6). If total lignin content is used instead of Klason lignin, the strict linearity is obscured. These results strongly indicate that the removal of lignin is responsible for the increase in swelling power obtained by bleaching and thus suggests that all of the changes in sheet properties must be in some way related to it.

Lignin is present in the fiber as an amorphous, inelastic network distributed through the fiber wall in varying amount. The experimental data obtained so far could be explained by the removal of lignin from the outer fiber surface, permitting increased numbers of carbohydrate-carbohydrate bonds to form between the fibers due to a decrease in the number of lignin-carbohydrate bonds per unit area (presumably less effective in holding the fibers together) brought about by lignin removal and concomitant fiber swelling. Removal of lignin throughout the fiber wall would also increase swelling by removing the restraint imposed on the fiber by the network of relatively inelastic lignin. Both mechanisms would account for the increase in compressibility noted on bleaching as in either case removing lignin would increase flexibility. There is no measurable change in compressibility between the bleached pulps themselves but this may be due to the insensitivity of the test; from a practical standpoint this difference may not be important.

Another factor which should be expected to have a great effect on compressibility is the presence of shives, which are highly lignified and quite stiff. Classification of the pulps, discussed in more detail later, suggests that a very significant change in the bigger shives is produced by bleaching; microscopic examination confirms this. Once the larger shives are eliminated, by even 1.5% hypochlorite treatment, it seems that further bleaching under the conditions of these experiments does not bring about compressibility changes, even though shifts in the fiber classification are produced. It would seem that the larger shives are a controlling factor in compressibility.

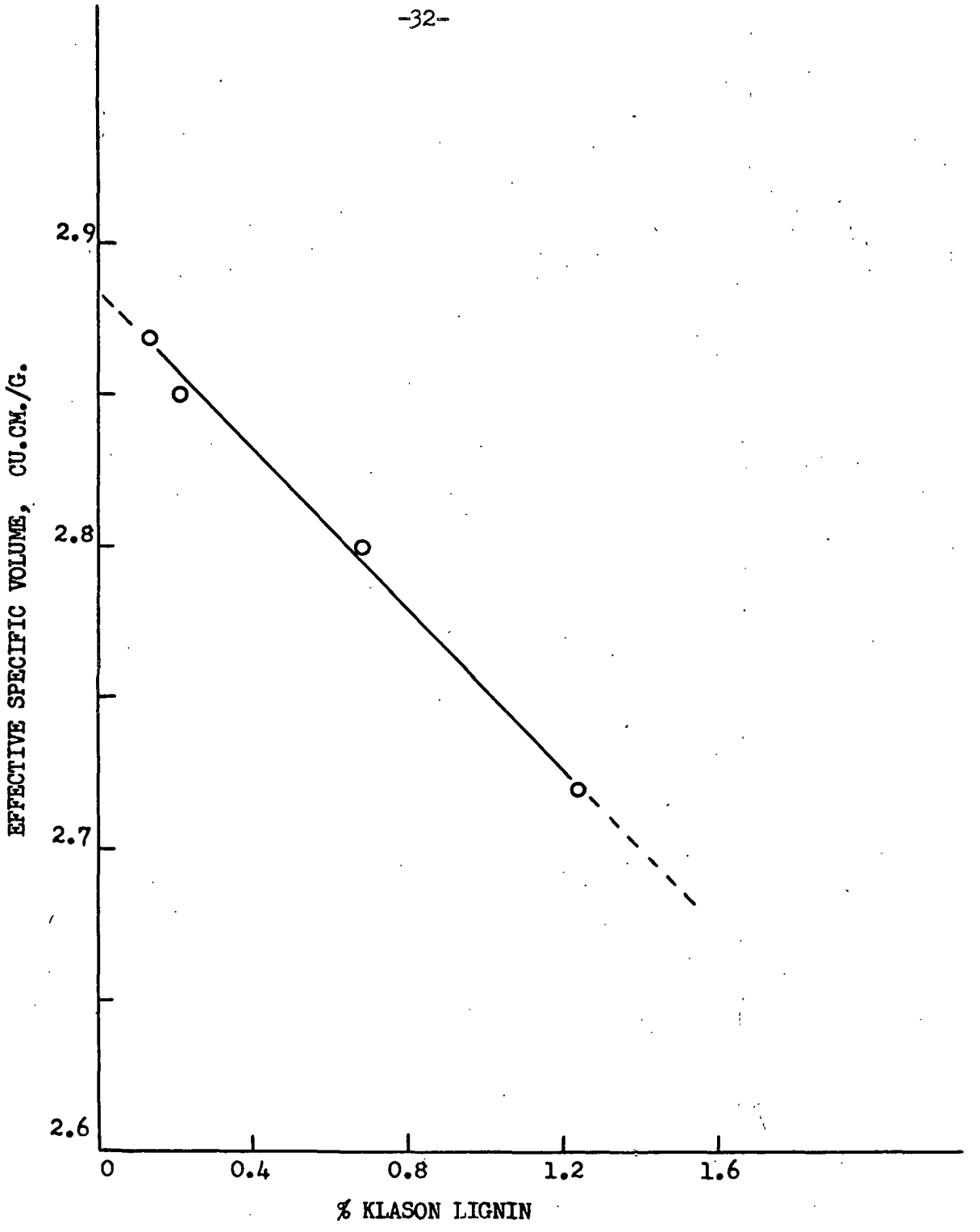


Figure 6. Swelling of Fibers as a Function of Klason Lignin Content

Breaking up shives into component fibers or smaller shives will have a very large effect on specific surfaces but may have only a minor effect on specific volume. This will be made clear by a consideration of Figure 7, page 39.

In a shive, the specific volume is made up of contributions from the fiber and the middle lamella; the surface area is that of the perimeter times the length of the shive. On hypochlorite bleaching, the lignin is removed and the fibers separate, increasing the surface area by a very considerable amount as all "inner" fiber surfaces are now included in the determination. On the other hand, the specific volume may not show a significant change as two effects are in operation--the removal of the middle lamella decreasing the volume, but the enhanced swelling of the cellulose increasing it.

If we neglect this effect and assume that swelling alone is responsible for the increase in surface area, it is possible to calculate the changes that should take place if two assumptions are made: first, the fibers are cylindrical in form, and second, that no change in fiber length is produced by bleaching.

Under these assumptions, the surface area should be a function of the square root of the fiber volume as the area depends on the diameter, and the volume on the diameter squared:

$$S = \text{Surface area} = \pi\, \underline{d}\underline{l} = K\underline{d}$$

$$V = \text{Volume} = (\pi \underline{d}^2/4)\underline{l} = K^1\underline{d}^2$$

$\underline{d}$ = Fiber diameter

$\underline{l}$ = Fiber length

Therefore, surface area = K^1 (volume)$^{1/2}$ as the d is the same in both equations, and changes in area should be related by the ratio of the square root of the fiber volumes.

If this relationship is valid, surface areas computed from changes in specific volume should be comparable with the experimentally determined values. There are only four pulps to compare, and one must be used as a basis for calculation. Compressibility has an unknown effect on the simple picture that has been developed. Therefore only pulps of identical compressibility values should be compared. The 1.5 pulp furnishes the initial conditions, and using the relationships developed previously, the calculated surface areas for the 3 and 6 pulps are 16,560 and 16,690 sq. cm./g., respectively. This compares favorably with the experimental values of 16,600 and 16,700 sq. cm./g., indicating that under these conditions the surface area increase concomitant with swelling is large enough to account for the experimentally measured increase.

If the 0 pulp values are used as initial conditions, the relationship does not hold as the calculated are about 1000 sq.cm./g. low. The compressibility of the 0 pulp is roughly 10% lower than the bleached pulps, which may be the reason for this discrepancy, as large, stiff shives are probably responsible for the lower compressibility and they will not fit the suggested picture.

The effect of fiber length on sheet strength cannot be overlooked as, all other things being equal, the longer the fiber, the greater its chance to form bonds with other fibers. The fiber length

distribution of the experimental pulps was determined on a Clark Classifier (33) using 14, 30, 50, and 100-mesh screens. The decrease in the coarser mesh (longer fiber lengths) fractions due to bleaching is obvious from the inspection of the data in Table VIII. Microscopic examination of the fractions was prompted by the difference in appearance of the coarse fractions in the classifier. In the case of the 0 pulp, fiber bundles or shives were present in large quantities, which was not true for the bleached pulps. The data, then, represent an effective fiber length and as the shives are broken down into their component fibers by delignification, the nature of the material retained on the screen changes. This has an important bearing on fiber-fiber bonding as shives cannot approach the amount or strength of bonding possible between two individual fibers because their high lignin content makes them very stiff and actually "covers" the underlying carbohydrate surface in many places. Burst tests on the fractionated pulps enforce this opinion. A twofold increase in burst is noted in the 14-30 mesh fraction when the 0 and 3 pulps are compared, and it is noted that a substantial reduction in shives has taken place. In comparing the 30-50 and 50-100 mesh fractions of these same pulps, a 10% increase in burst, with practically no change in shive count, is noted. Apparently the removal of lignin from individual fibers is also a factor in the strength development noted.

MICROSCOPIC STUDIES

SWELLING STUDIES IN CUEN

The nature of the physical changes produced by bleaching and the

TABLE VIII

PROPERTIES OF FIBER FRACTIONS

Fraction		Apparent Fiber Length Distribution, weight %				Burst Factor, g./sq.cm/g./sq. m.			Shive Count[1]	
% Hypochlorite		0	1.5	3.0	6.0	0	3	ratio,3/0	0	3
Thru	Retained									
0	14	1.1	0.5	0.2	0.1	-	-	-	-	-
14	30	19.3	18.0	8.6	6.4	0.129	0.305	2.4	27.2	4.0
30	50	48.5	51.2	61.4	63.7	0.289	0.320	1.1	9.7	8.4
50	100	27.3	26.8	25.2	22.4	0.332	0.375	1.2	4.9	3.5
100	--	3.8	4.1	4.6	7.4	-	-	-	-	-

[1]Number per cent of bundles consisting of two or more fibers

rather striking lack of chemical effects suggested an analogy between bleaching and beating. To investigate the effects suggested by the anology, microscopic examination of the bleached pulps was undertaken. Evidence of fibrillation on the fiber surfaces and dissolution without concomitant ballooning in cupriethylenediamine (cuen) are characteristic of most beaten, bleached pulps. Lack of these effects would indicate that hypochlorite bleaching achieved the same (or similar) end result as beating in a more subtle fashion.

The first investigation of the bleached pulps indicated that fibrillation was not pronounced enough to be readily visible under the light microscope. Therefore, the swelling behavior of the pulps was carefully examined. It was known from the viscosity studies that the pulps were difficult to dissolve in cuen unless a two-stage solution procedure was used. Microscopic examination showed that most of the individual fibers could swell and dissolve in 0.25 M cuen. Shives resisted solution. The behavior of a great number of fibers was observed and two conclusions reached: all fibers exhibit the characteristic "ballooning" of unbeaten pulps indicating that the outer wall of the fiber was not split open, and the rate of balloon formation is a function of the severity of the bleaching stage, suggesting the removal of some component that restricts swelling or weakening of the outer wall by degradation; this parallels the results obtained by Carpenter and Lewis (34) on aspen soda pulps. The experimental observations are presented in the following table.

TABLE IX

BEHAVIOR OF PULPS IN CUEN

Hypochlorite, %	0	1.5	3.0	6.0
Solution time, min.	<25+	12	4	1.5
Ballooning	yes	yes	yes	yes

Removal of lignin is most probably responsible for these effects; its removal from the surfaces of the fiber or from throughout the cell wall could explain the increased rate of swelling and attendant decrease in solution time. A small amount of hemicellulosic material is removed by bleaching, but is probably too insignificant to account for the marked changes that have occurred.

REVIEW OF FIBER STRUCTURE

A brief review of fiber morphology will clarify the reasoning underlying the series of experiments that lend credence to the idea that the removal of lignin, primarily from the surface of the individual fibers and the break-up of shives, is primarily responsible for the strength improvement experienced with hypochlorite treatment, and explain why strength increases with increasing severity of bleaching. Figure 7 is an idealized concept of wood fiber structure showing the architecture of an individual fiber and its relationship to neighboring cells (35). The different structural features behave differently in their response to chemical attack, which led early investigators to assume that each "layer" had its own peculiar chemical composition in terms of the lignin, cellulose, and hemicellulose that are ordinarily measured on wood and pulp samples. A variety of techniques in the hands of many investigators

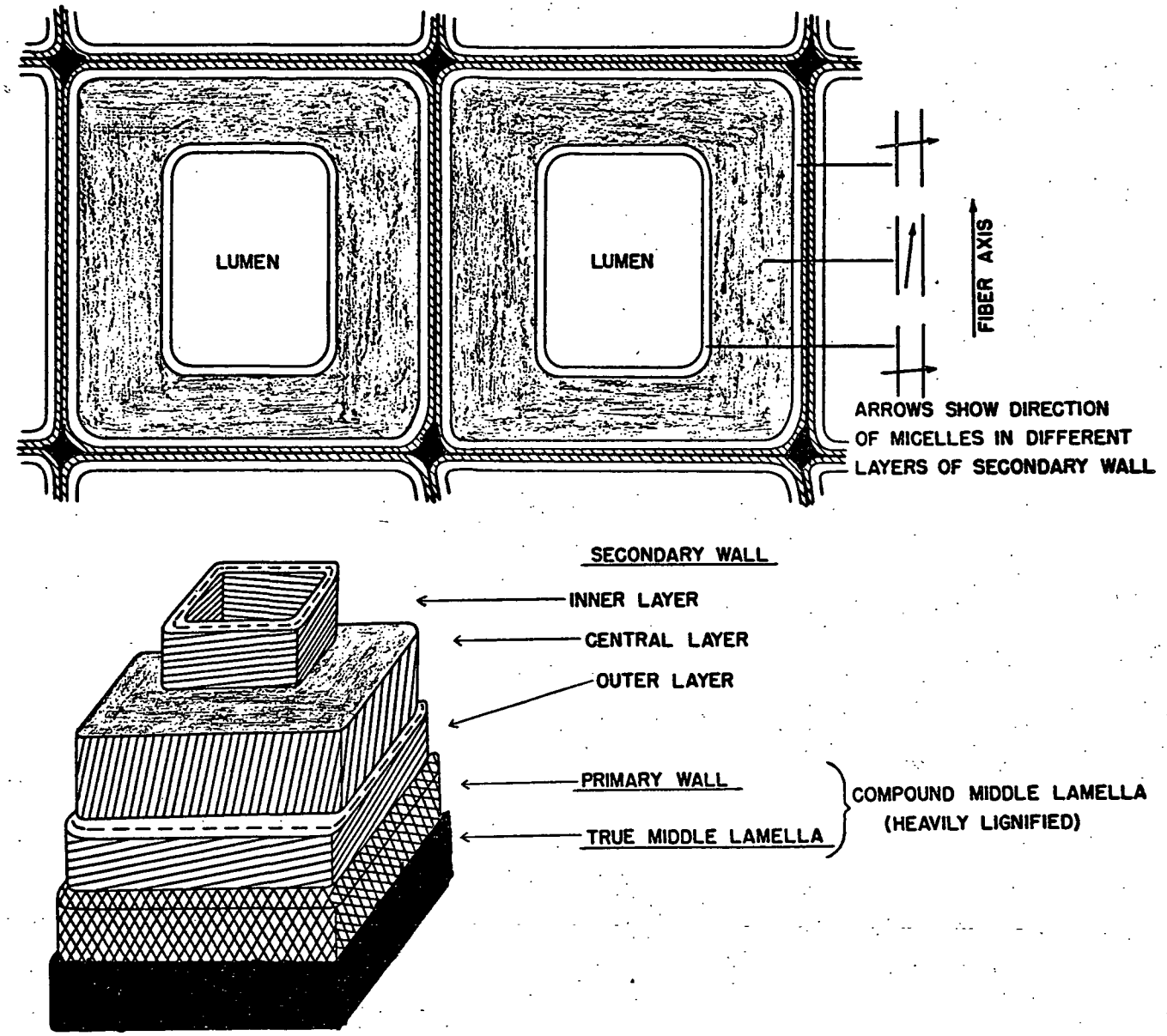

LUMEN
LUMEN
FIBER AXIS
ARROWS SHOW DIRECTION
OF MICELLES IN DIFFERENT
LAYERS OF SECONDARY WALL
SECONDARY WALL
INNER LAYER
CENTRAL LAYER
OUTER LAYER
PRIMARY WALL
TRUE MIDDLE LAMELLA
COMPOUND MIDDLE LAMELLA
(HEAVILY LIGNIFIED)

Figure 7

has enabled us to construct a general outline of the compositional changes through the cell wall.

In a classic work, A. J. Bailey (36) separated the middle lamella (probably the compound middle lamella) from Douglas-fir by microdissection and then analyzed it for lignin and pentosans by micro methods. He concluded that the middle lamella was 71% lignin and 14% pentosan. Harlow (37) studied the solubility of wood sections in 72% sulfuric acid and concluded that the middle lamella was highly lignified. The nature of the cell walls was investigated by Lange (38) using physical methods. He confirmed the nature of the compound middle lamella and also indicated that the outer layer of the secondary wall is lignified to a significant extent, and that carboxyl groups and hemicelluloses are present in highest concentration at the outer walls of the fiber decreasing to a low value near the lumen.

Several workers have confirmed the general trends of these results by other techniques: Dolmetsch (39) used preferential solubility to establish that the outer wall of the fiber is rich in pentosan; Haas (40) studied the differences in behavior of the fiber wall on acetylation and xanthogenation, before and after removing material of low D.P. (150) and concluded that the outer wall was rich in hemicelluloses.

Dadswell and Ellis (41) studied the 72% acid solubility of a number of woods and observed that the concentration of lignin in the secondary wall must be quite low. Additional evidence for a high lignin content in the outer layers of the fiber wall has been obtained from the examination of lignin determination residues by Dolmetsch (39), Jayme and

von Köppen (17), and Keeney (42). Their results indicate that for at least sulfite and NSSC pulps, lignin must be present in the outer walls of the fiber in high enough concentration to form a continuous network that shows the morphology of the outer portion of the fiber.

Summarizing these results in a graphical presentation of the distribution of components through wood fibers, we may represent the situation as follows:

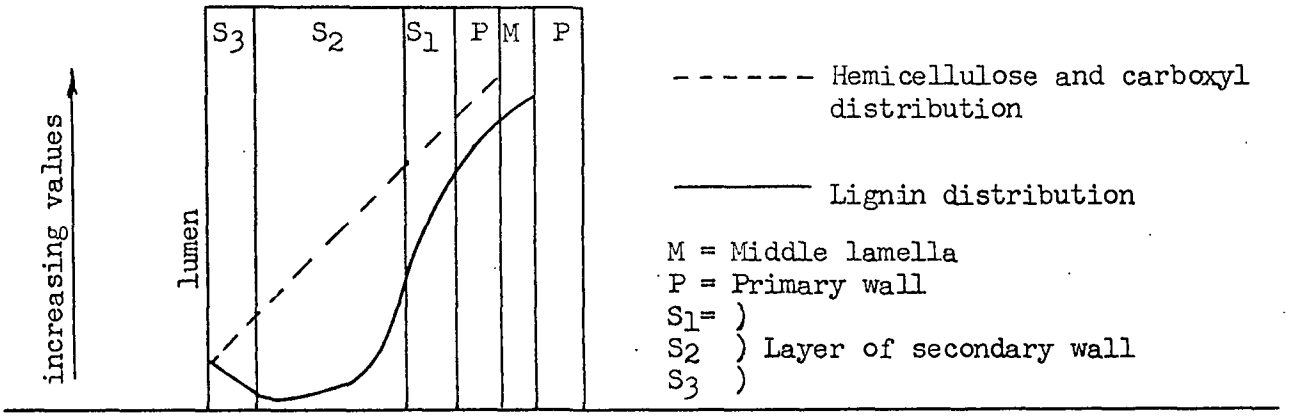


Figure 8

Idealized Distribution of Components
Through Fiber Walls

The pertinent conclusions to be drawn from the data just discussed are: lignin is concentrated in the outer walls of the fiber (P, S_1) to such an extent that it can be isolated as a coherent structural residue after hydrolysis of the polysaccharides; the outer wall is rich in hemicelluloses and carboxyl.

KLASON LIGNIN "RESIDUES"

Klason lignin determinations were carried out on the 0, 1.5, 3, and 6 pulps. The insoluble residues (Klason lignin) were carefully filtered off at the finish of the determination and examined while still wet, under the microscope. The vast difference in appearance caused by bleaching is seen when the photomicrographs of the 0 and 6 pulp residues are compared. The results prove conclusively that the "fibrous" nature of the residue from unbleached NSSC reported by Keeney (42) carry through the bleaching stages. Not evident in the photomicrographs is the three dimensional character of the residues. They have the appearance of hollow tubes. In Figure 9, residues left by fiber bundles seem to predominate and very few residues attributable to individual fibers are present, while the residue from the 6 pulp, Figure 10, shows that these are very nearly destroyed by intensive bleaching. However, while the shives seem to contribute to a major part of the Klason lignin (the 0 pulp, 14-30 mesh fraction contains 3% lignin compared to 1.2% for the whole pulp) individual fibers do possess "structural" residues. Figure 11 is a series of photomicrographs taken at about 500 diameters of the lignin residues from the 0 pulp, 50-100-mesh fraction which contains few fiber bundles. A ruptured residue of a vessel segment showing many structural features is present. An apparent "porosity" can be noted in parts of the cell wall, indicating differences in the thickness of the lignin. The residue obtained from shives shows individual fiber walls, probably the "compound middle lamella." These structural residues are resistant to prolonged treatment with 72% sulfuric acid, and if rehydrolyzed with acid, a negative Molisch test is obtained. They are

Figure 9

Klason Lignin Residues, x 150

O Pulp

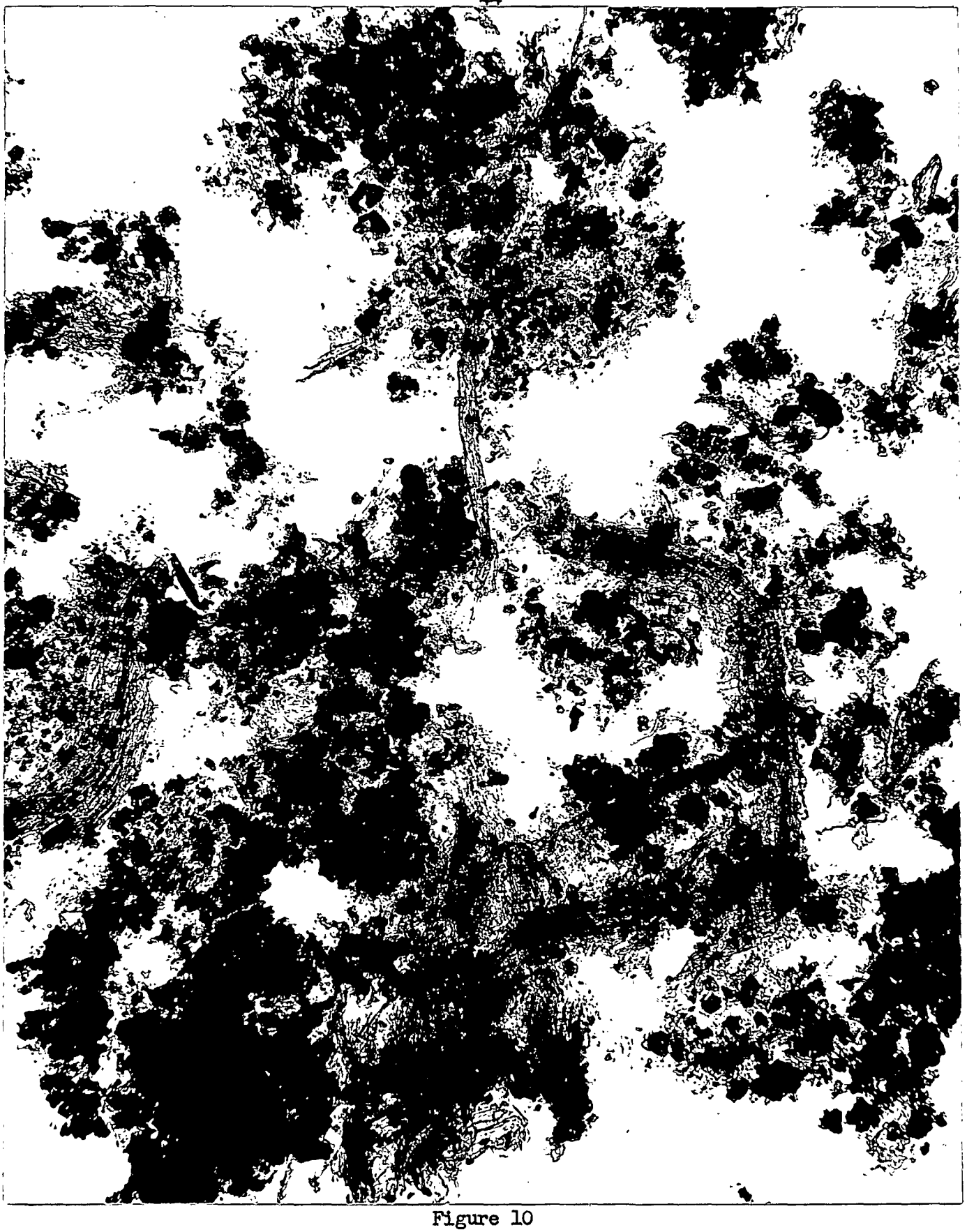
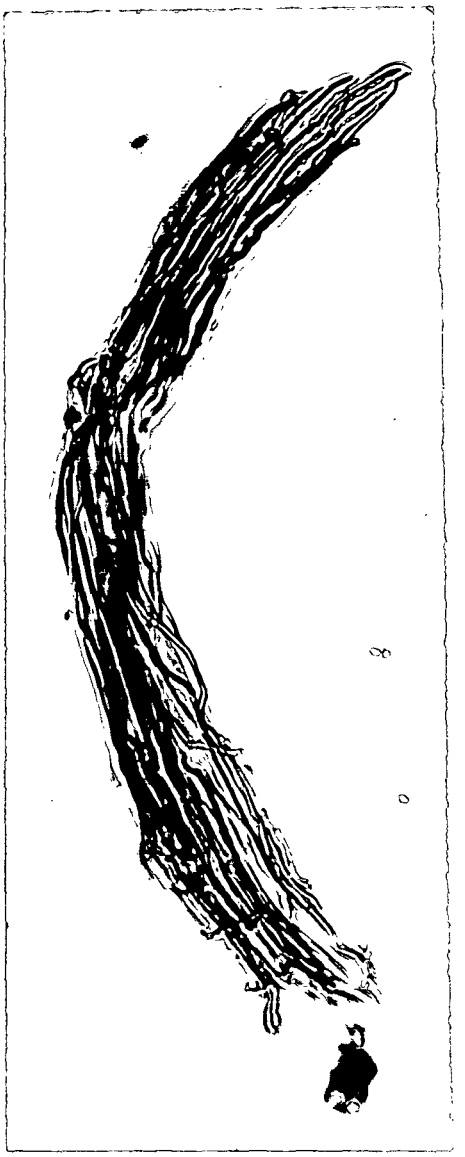


Figure 10

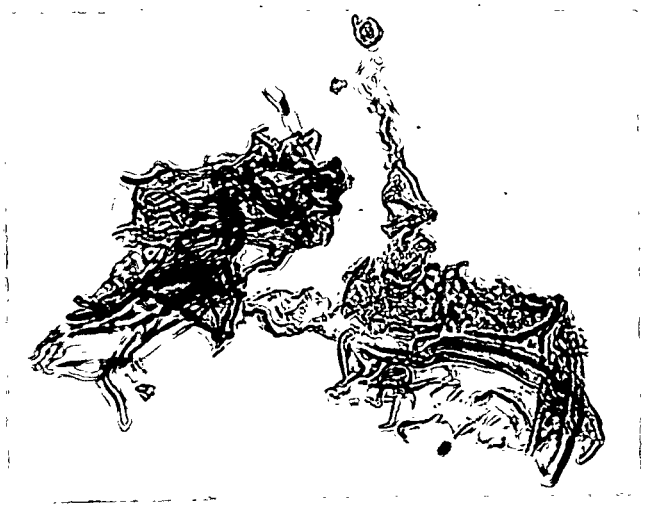
Klason Lignin Residues, x 150

6 Pulp

Fiber Fragments and Shives
x 400



Shive x 500



Vessel Fragment x 400

Figure 11

Klason Lignin Residues

the analytically defined Klason lignin. Even the dark amorphous appearing masses in Figure 10 have structure when examined at high magnification. They were probably formed by the folding and collapse of the lignin residues during the hydrolysis with 3% acid, carried out at the boiling point; a microscopic examination of the 72% acid stage shows no such effects. Carrying out the hydrolysis in a water bath held at the boiling point minimizes the damage to the residues by eliminating vigorous convection currents. The clear image of the external surface of the fiber found in these residues is confirmatory evidence for the concept of a high lignin contentration at the surfaces of the fiber. Removing this material would increase the swelling of the fiber and increase the possible fiber-fiber bonding. These observations, in conjunction with the physical and chemical data, make it probable that the removal of lignin from the surfaces of the fibers and the break up of shives can account for all of the changes in properties noted. It would seem unlikely that the small amount of lignin present in the interior of the fiber would have a great effect, but some removal may occur here as well, enhancing the changes.

CARBOXYL DISTRIBUTION

A qualitative study of the carboxyl group distribution through the fiber was made by staining the fibers with the carbinol base of crystal violet (method of Lange) and observing the distribution of dye through the fiber cross section. The base does not react with hydroxyl groups, but is converted to the blue acid form by carboxyl groups. The results indicate that aspen is similar to birch and spruce in carboxyl

distribution (45), high at the outer walls and decreasing to some low value near the lumen as indicated by the distribution of blue color in the fiber cross section.

SULFONIC ACID DISTRIBUTION

An azo dye, p,p'-diazodimethylaniline has been shown to be specific for the sulfonic acid group in pulp (46), staining fibers red when such groups are present. No color is produced with kraft pulps, for example.

Samples of the 0 through 6 pulps were stained with the dye to determine if a preferential distribution of sulfonic acid groups existed (it has been demonstrated that sulfonation in a sulfite cook proceeds from the middle lamella through the fiber wall, and that kraft liquors attack the wood in a more uniform way). The individual fibers did not take appreciable amounts of color, but the shives stained a bright red, indicating high concentrations of sulfonic acid groups. The possibility exists that the lignin in the individual fibers is highly sulfonated, but is present in such small amounts that little color is evident. As the shives are resistant to bleaching, the increase in sulfur content compared to lignin may possibly be due to the high sulfonic acid content of the shives. The indications are that the sulfonation did not take place in a uniform manner, but further work would be necessary to establish this point with certainty.

LIGNIN DISTRIBUTION IN PULPS

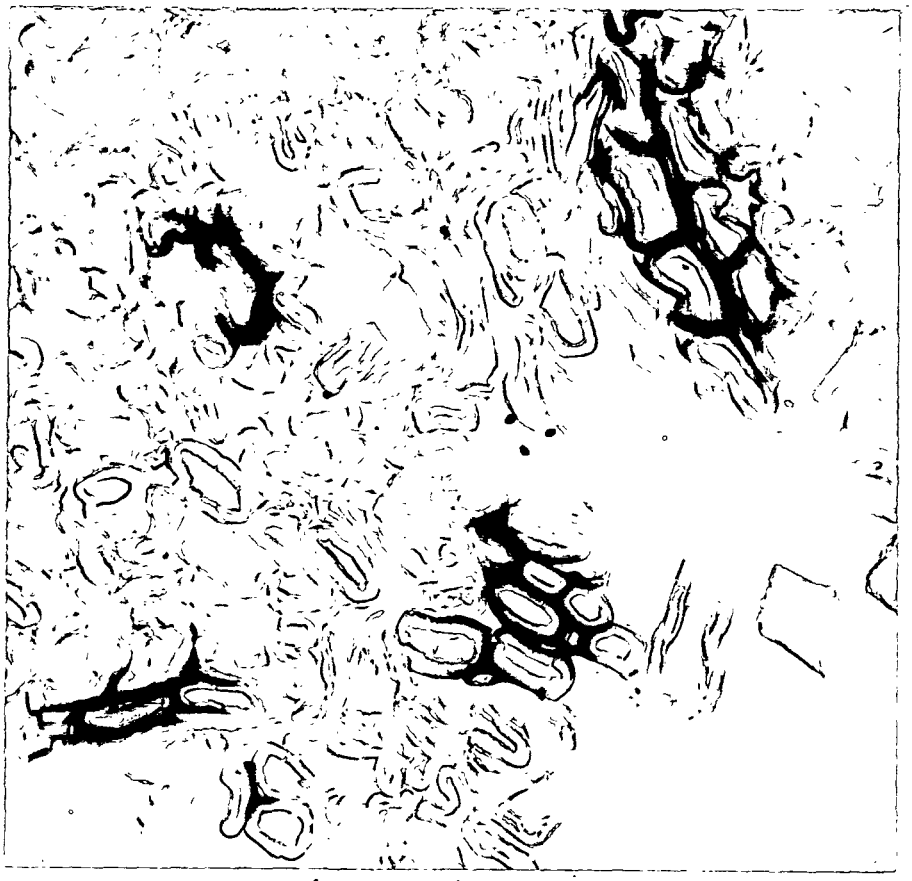
An attempt was made to determine the distribution of lignin through the fiber walls before and after hypochlorite treatment by

staining fiber cross sections with malachite green. The concentration in the fibers was so low that even under conditions of maximum contrast (red filter) no differences were observable between the 0 and 6 pulps. Only shives stained to an appreciable extent; the photomicrographs in Figures 12A and 12B were taken at several magnifications to show typical fields. A qualitative idea of the lignin distribution of the shives can be obtained from the photomicrographs at the bottom of the page. Dark areas represent high concentrations of lignin. It will be noted that the area near the fiber lumen is much lighter than near the outer wall, which is consistent with the picture of fiber architecture that has been presented. A more refined technique would be necessary to detect the apparently minor amount of lignin distributed through the outer layer of the secondary wall of the fibers. A small amount must be present to give rise to the structural residues from individual fibers shown in Figure 9. Nonuniformity of both cooking and bleaching make it possible that these residues came from the fibers that suffered minimal attack during processing.

BLEACH LIQUOR ANALYSIS

COLLECTION OF LIQUOR ON SAMPLES

The material balance on the bleaching stage and the chemical studies on the bleached pulps indicate that very little material besides lignin degradation products should appear in the bleach liquor. This was confirmed by measuring the total organic matter in an aliquot of the concentrated liquor and also before determining carbohydrates. Only the 1.5 and 6 pulp bleach liqurs were investigated, but in both cases the

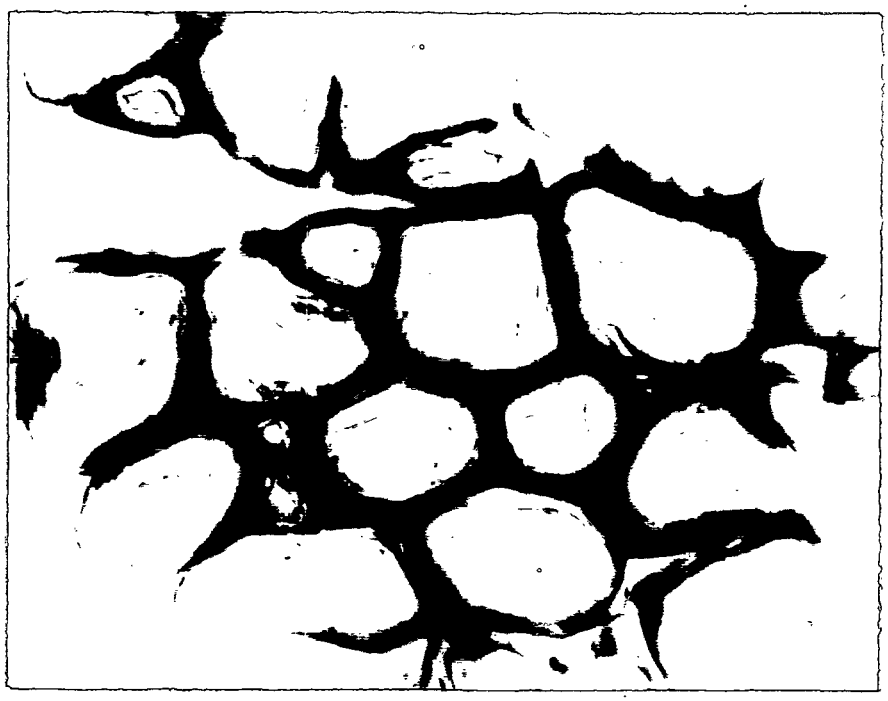


6 Pulp x 400

0 Pulp x 500

Figure 12 A

Lignin Distribution As Shown By
Malachite Green Stain



6 Pulp x 950

0 Pulp x 950

Figure 12 B

Lignin Distribution In Shives As Shown By
Malachite Green Stain

carbohydrates were only about 2% of the total organic matter expressed as carbon. The amount is not precise, as it was necessary in both cases to neutralize the liquor with sodium hydroxide and evaporate it to dryness *in vacuo* to remove the hexyl alcohol that was used as a defoamer in the liquor concentration. The dry powder was dissolved in 10 ml. of water and a 1-ml. aliquot subjected to the wet combustion.

The excess hypochlorite at the end of a bleaching period was destroyed by sodium sulfite to eliminate unwanted side reactions between the liquor and oxidation products, and the pulp was dewatered on a Buchner funnel. After a consistency of *ca* 25% was reached, the pulp was removed from the funnel and reslurried in filtered tap water, then refiltered. Washing was carried out until 9 liters of liquor were collected for each bleaching determination. The initial wash was yellow in color, the last, colorless. These liquors were filtered through a medium porosity fritted glass funnel to remove any fiber debris and then stored under toluene at 5°C. until required for analysis.

PREPARATION OF SAMPLES FOR ANALYSIS

The initial step in analysis was concentration of the liquors to a small volume (10-15 ml.) carried out *in vacuo* at 25°C. This concentrated liquor was chromatographed on Whatman number 1 filter paper in 10-3-3 and 9-2-2 systems. No simple sugars were present; *p*-anisidine hydrochloride was used as the developing spray, and it did show some spots whose color indicated they were probably of noncarbohydrate origin. As it is impossible to characterize an unknown compound from only its position

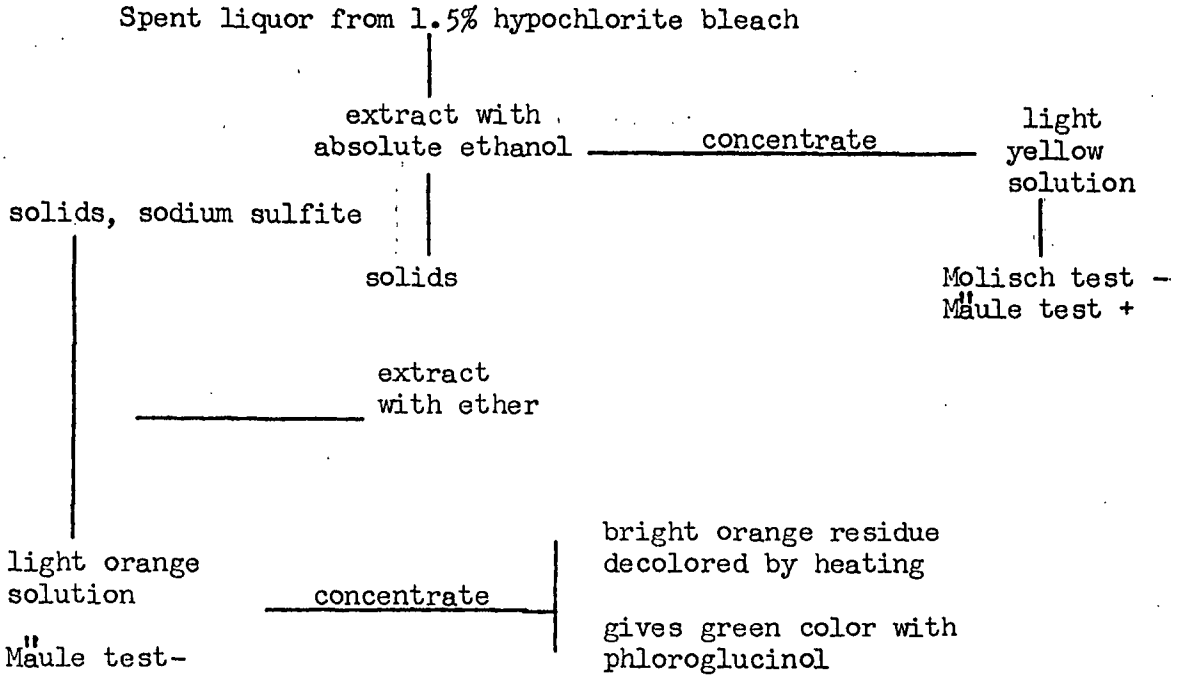
on a chromatogram, these materials were not investigated further. They would have to be isolated and identified by preparation of derivatives.

The liquors gave positive Molisch and Mäule tests, indicating that carbohydrates and some form of syringyl substances were present. An attempt at fractionating the liquors into alcohol and ether-soluble fractions met with limited success as sodium sulfite, being slightly soluble in alcohol, was carried into all of the fractions in amounts much larger than the organic materials. Some interesting color reactions were observed, and are reported in Table X.

It was apparent that hydrolysis of the liquors would yield interesting information, as the composition of the carbohydrate fraction could be determined. The hydrolysis was carried out with sulfuric acid as discussed in the Experimental Procedures, p. 80. It was complete as far as carbohydrates were concerned as only simple sugars appeared in the hydrolyzate. Only xylose, galactose, arabinose, and glucose were identified in the hydrolyzed liquors. They were determined quantitatively by the method of Pridham (discussed on p. 99); the results are presented in Table XI.

TABLE X

QUALITATIVE FRACTIONATION OF SPENT BLEACH LIQUOR



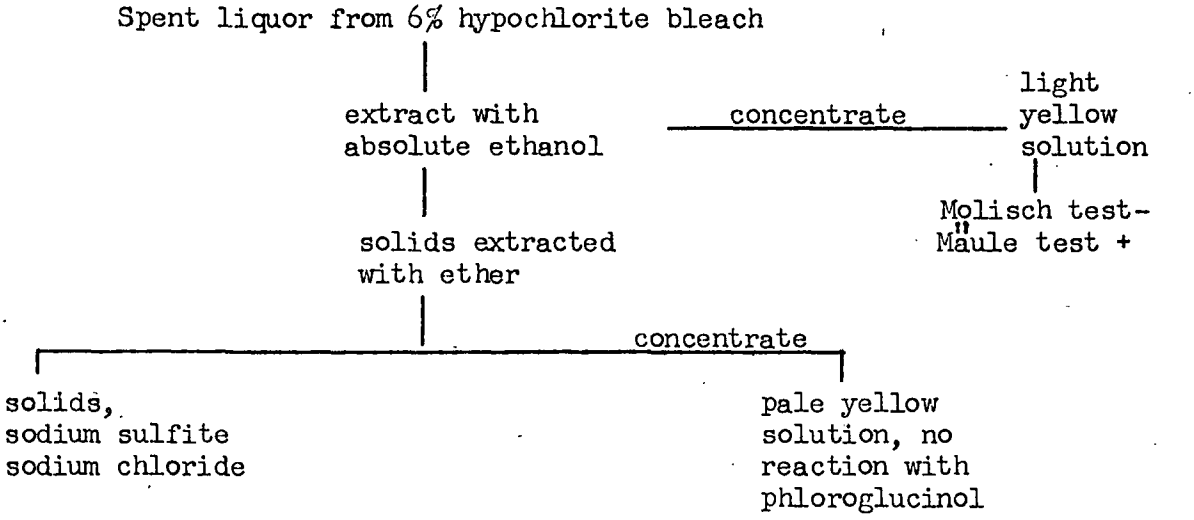


TABLE XI

COMPOSITION OF CARBOHYDRATE FRACTION OF BLEACH LIQUORS FROM 1.5 AND 6% HYPOCHLORITE BLEACHES

	Boehm's Chlorination and Extraction Stage Liquors		1.5	6
	Cl_2	NaOH		
Xylose	30.9	68.0	69.6	76.9
Arabinose	41.5	16.8	12.9	7.7
Galactose	21.0	12.5	17.5	15.3
Glucose	5.2	1.6	Trace	Trace
Mannose	--	--	--	--

ANALYSIS OF THE CARBOHYDRATE PORTION OF THE BLEACH LIQUORS

The agreement in analysis of the components removed by the caustic-extraction stage on one hand and the hypochlorite stage on the other, is striking. It suggests that possibly the high pH of the hypochlorite stage acts as a mild alkaline extraction as far as the carbohydrates are concerned. The yield of carbohydrate is, of course, very much higher for caustic extraction, where they are roughly 10% of the total carbon [based on 4.6% lignin and 0.9% carbohydrate removed by the extraction stage (3)]. It is also possible that these hemicelluloses are imbedded in the lignin and are liberated as the lignin is removed by the caustic-extraction or hypochlorite stage.

An even more interesting picture is reflected if we consider the "hemicelluloses" removed in the chlorination stage, again using the data of Boehm (3). It is then apparent that the amount of xylose in the liquors increases as each stage of the bleaching process is carried out. Pro-

cessing also appears to be more selective in that less and less glucose appears; galactose shows a marked decrease between the chlorination and extraction stages as does arabinose. These results suggest that a nonuniform distribution of hemicellulosic sugars probably exists in the cell wall, and one would suspect that arabinose and galactose are predominant in the most accessible portions of the wall or most readily hydrolyzed.

The "acid" fractions of the hypochlorite bleach liquors here defined as substances that move in the 9-2-2 solvent system but not in the 10-3-3 system, were investigated with several spray reagents. Phenols were detected in both the 1.5 and 6 liquors, but four distinct bands were present in the 1.5 liquors and only one in the 6. This was probably due to the secondary reactions in the 6 liquor - those of fragments split off the lignin molecule by hypochlorite - destroying the initial reaction products. This occurs to a much lesser extent with the less concentrated hypochlorite solutions. The phenolic constituents were detected with diazotized p-nitroaniline coupled with alcoholic sodium hydroxide. A compound that gave a red color with p,p'-diazodimethylaniline was detected in the 1.5 liquor but not the 6. This material is presumably a sulfonic acid.

CONCLUSIONS

Hypochlorite as the last stage in a CEH bleaching sequence for preparing a fully bleached NSSC aspen pulp was investigated.

The bleaching was carried out in a system buffered to pH 10.0-10.5 with sodium hydroxide at 10% consistency and 40 ± 1°C. Lignin content was determined on the experimental pulp and several commercial pulps at the end of their respective extraction stages for comparison purposes. The stage accomplished its major purpose, brightening the pulp, with minimal damage to the carbohydrate fraction of the pulp and nearly quantitative removal of the lignin.

A brief tabulation of the analytical data for the pulp from the extraction stage and pulp bleached with 6% hypochlorite (most severe bleach) will facilitate the discussion of the experimentally observed changes produced by the action of hypochlorite on the pulp.

TABLE XII

COMPARISON OF PULP ANALYSIS
BEFORE AND AFTER 6% HYPOCHLORITE TREATMENT

Hypochlorite, %		0	6
I	Lignin (Klason and soluble), %	1.61	0.25
	Sulfur, %	0.13	0.06
	Pulp D.P.	1960	1330
	"Carboxyl" in pulp, %	16.3	15.0
	Carboxyl in A.R.C.	3.1	4.1
II	5% KOH hemicellulose, %	14.1	14.0
	16% KOH hemicellulose, %	10.1	10.6
	A.R.C.	74.2	74.6
	95% Ethanol extractives, %	0.6	0.8
	Hemicellulose D.P. 5% KOH	139	139
	16% KOH	150	146

The table is divided into two sections. In I, there are significant changes, and in II there are no significant changes produced by the action of hypochlorite on the pulp. It many be seen that lignin removal becomes almost quantitative, sulfur content of the pulp is decreased, and "carboxyl" content of the pulp is decreased by the action of hypochlorite.

The amount of carbohydrates and extractives is practically unaffected by the action of hypochlorite. A material balance confirmed that lignin was the only pulp component removed in quantity and analysis of the bleach liquor where carbohydrates represent only 2% of the organic carbon present, substantiate these results.

The bleached pulps were refined in a Jokro mill to evaluate their physical properties. Handsheets were made at various beating times for

each of the bleached pulps and evaluated for breaking length and bursting strength. By plotting sheet density as a function of beating time a family of curves with per cent hypochlorite applied in the third stage as a parameter, was formed (cf. Figure 2). Breaking length was plotted against sheet density and all points, either for different amounts of bleaching or different amounts of beating, fell on the same line (cf. Figure 3), indicating sheet density was a controlling factor in sheet strength.

The apparent distribution of fiber lengths as determined by screen classification was shifted in the direction of shorter fibers by increased bleaching (Table VIII).

Filtration resistance of the pulps increased as bleaching conditions were made more severe (Figure 5) as did the specific surface and effective specific volume of the fibers (Table VII). Compressibility showed a 10% increase comparing the 0 and 1.5 pulps, but further increases in hypochlorite treatment did not cause further increases.

Microscopic examination indicated that most of the lignin and sulfonic acid groups in the pulp at the end of the caustic-extraction stage or the hypochlorite stage are present in the shives.

The experimental evidence that has been presented permits comparison between NSSC and other pulping processes as well as the deduction of a possible mechanism that can explain all the effects observed.

The decrease in sulfur content and "carboxyl" are related by theoretical considerations. It was pointed out in the body of the

report that the method of measuring carboxyl is not specific, but is affected by the over-all ion-exchange value of the pulp. This apparently does not introduce any difficulties in studying the bleaching of chemical pulps, but does have an effect in the present work. The sulfur groups in the lignin can enter into the exchange reactions in a manner analogous to that of the carboxyl groups and are thus measured in the determination. It is possible to correct for the contribution of these groups to the over-all ion-exchange value by assuming that each sulfur atom is equivalent to a carboxyl group in exchange capacity, but it is also probable that the lignin has other groups that contribute and cannot be accounted for by the sulfur analysis. By isolating the A.R.C. fraction from the pulp and determining its carboxyl value, an idea of the effect of hypochlorite on the cellulose fraction of the pulp was obtained. The value shows an increase with increasing severity of bleaching which is typical of the behavior of cotton and chemical pulps. The drastic alkaline- extraction stages used to isolate A.R.C. probably permit the chain cleavages made possible by the presence of electronegative groups to occur. Therefore, the carboxyl values may be slightly higher than those for cellulose not subjected to an extraction stage, but it is probable that the alkaline conditions of the hypochlorite stage itself are enough to cause all of the possible cleavages.

If the total ion-exchange value of the pulp was corrected for the contribution of the sulfur groups in the lignin and the carboxyl groups in the A.R.C., the remainder was constant within experimental error; this should represent the contribution of the hemicelluloses.

Lignin showed a very interesting distribution through the fibers. Staining with malachite green, through not a precise technique, indicated the major portion of lignin left in the fiber after the caustic-extraction stage and the hypochlorite stage was present in the middle lamella region of the shives that were present. When the insoluble residue of the Klason lignin determination was examined microscopically before drying, the lignin "skeletons" of individual fibers and shives were observed; the skeletons from fibers showed a large amount of detail, suggesting they originated from the outer walls of the fiber. The picture of lignin distribution through fibers is consistent with this belief (36-42). The presence of these skeletons suggests that NSSC is more similar to sulfite than sulfate, if the work of Jayme and von Köppen (17) is taken as a basis for comparison.

A hypothesis that can explain the strength improvement caused by bleaching will be discussed at this time as it is on sounder ground than some of the other comparisons.

Analysis of the bleached pulps show that hemicelluloses were not removed or degraded and while degradation of the cellulose occurs, it does not have an adverse effect on sheet strength. Therefore, it would seem that the only significant variable in the measurements--the lignin content--might be responsible for the changes in physical properties.

The key to this suggested relationship between lignin and strength may be in the effect of lignin on swelling as measured by specific volume. It was shown that a linear correlation between lignin and specific volume exists. Lignin, being nonswelling and inelastic, in-

hibits fiber swelling whether it is present as a continuous network, throughout the fiber, primarily on the fiber surface, or as the complete middle lamella in shives. From the standpoint of the microstructure of these NSSC pulps, it has been shown that the largest portion of the lignin is present in the shives, and some must also be associated with the outer surface of individual fibers. This may be predominantly primary wall lignin as the pulps have been gently handled, eliminating the mechanical erosion that strips off this wall in commercial pulps (46) or it may be in the outer layer of the secondary wall, or both. Removal of any lignin therefore aids swelling.

For pulps having the same compressibility, the increase in surface area concomitant with bleaching calculated from the changes in specific volume checks satisfactorily with the experimentally determined values of surface area. This relationship does not hold if a significant compressibility change occurs, presumably because this signals the disintegration of large, stiff, shives, which cause a significant change in area but have little effect on specific volume. Surface area is a measure of the area available for bonding, and as it increases, sheet strength should also increase. This was demonstrated for the case of the series II pulps.

Bleaching by removing lignin from the outer surfaces of the fiber should make the pulp easier to beat as the amount of mechanical work necessary to bring about strength improvement is decreased. Removal of the highly lignified primary wall is necessary for adequate fiber-fiber bonding and can be done either by mechanical or chemical means. If ease of beating is measured by the time required to reach a given sheet

density, then the experimental data is in accord with this concept. Another interpretation of the data is that bleaching gives the pulps a head start in strength development as they have higher zero interval sheet densities than the unbleached pulp, but this appears to be restating the first explanation in a slightly different manner.

A spot check made on the 0 and 3 pulps suggests the relative importance of delignification of individual fibers and shives in producing increases in sheet strength. In the long fiber fractions (made of long fibers and "long" shives) bleaching with 3% hypochlorite reduced the shives by a factor of seven and doubled the burst factor. In the shorter fiber fractions, the change in shive content was relatively small and only a 10% increase in burst factor resulted. Thus, both types of delignification have an effect, but the disintegration of shives is the most significant in an individual fiber fraction. This may come about because lignin-carbohydrate bonds are intrinsically weaker than carbohydrate-carbohydrate bonds, or more probably, that the maximum bond density (number of bonds per unit area) possible at a lignin-carbohydrate interface is significantly less than at the carbohydrate-carbohydrate interfaces; removing lignin increases the possibility of carbohydrate-carbohydrate bonding. The increase in available carbohydrate surfaces will be much greater if a shive is separated into its components than if an individual fiber is further delignified. Staining studies indicated that the individual fibers were quite free of lignin, so the increase in carbohydrate surfaces is due to a combination of a small amount of lignin with the resulting increase in swelling. On the other hand, disintegration of a shive can very conceivably increase

its area by several hundred per cent. The relative magnitude of these two effects on the whole pulp depends on the amount of each fiber fraction present and any interaction between the fractions.

To summarize, the chemical and physical changes produced by hypochlorite bleaching of NSSC pulps with available chlorine concentrations of zero to 6% can be almost entirely explained by the removal of lignin. Theoretical reasons for the observed strength improvement have been discussed; removal of lignin from individual fibers and the disintegration of shives are probably responsible. The chemical effects can be explained as a result of changes in the amount of sulfur groups which can enter into ion-exchange reactions, and are associated with the lignin.

Some parallels between NSSC and other pulps may be drawn from the data, but differences in experimental conditions make anything other than suggested correlations impossible.

The behavior of the hemicellulosic fraction of bleached NSSC pulps appears to be similar to that of sulfite rather than sulfate pulps based on a comparison of the present experimental results with those of Meller (46). He found that the pentosans removed by 7% sodium hydroxide in sulfite pulp was unchanged, but that the sulfate pulp decreased on hypochlorite treatment. No information on degradation was obtained, but the results are comparable to a greater extent than those of the usual bleaching studies as very high hypochlorite concentrations were used. The pentosan content of both sulfite and NSSC is relatively unaffected by bleaching.

The distribution of carboxyl groups in NSSC aspen pulp is qualitatively the same as that reported for birch and spruce pulps (43). The highest concentration of carboxyl occurs at the outer wall of the fiber, and as the carboxyl groups are predominantly associated with the hemicellulose fraction of the pulp, the major portion of the hemicelluloses should be located near the fiber surface. This suggests that the small amount of hemicellulosic carbohydrate found in the spent bleach liquor could have been removed with the lignin, either because it was embedded in a lignin matrix or a lignin-carbohydrate bond existed.

Another explanation for the presence of the hemicelluloses in the bleach liquor is that the conditions of the stage were alkaline enough to act as a mild caustic extraction, removing a small amount of low D.P. material.

SUMMARY

The effects of hypochlorite as the third stage in the bleaching of NSSC aspen pulp have been investigated. Commercially used hypochlorite concentrations produced only small changes in chemical and physical properties of the bleached pulps; therefore, it was necessary to prepare a series of pulps bleached with increasingly higher amounts of hypochlorite to establish the direction and magnitude of these changes. The fixed hypochlorite stage conditions were chosen to approximate commercial operation. Bleaching was carried out at 10% consistency, 40 ± 1°C., pH 10.0-10.5 for 2 hours. Available chlorine was varied between 0 and 6% on the basis of the pulp charged to the stage.

The bleached pulps were characterized by chemical analysis, determination of specific surface, specific volume, and microscopic examination. A beater evaluation was also carried out on each bleached pulp to determine changes in handsheet strength and "ease of beating." From the chemical analysis, it was established that lignin was the only pulp component removed by hypochlorite in appreciable quantity. The carbohydrate fractions of the pulp were not changed in amount so far as could be determined by measuring hemicellulose and A.R.C. yields on the bleached pulps. Some degradation of the pulp was produced by bleaching, lowering the D.P. from an initial value of 1960 to 1330 for the severest condition. Hemicelluloses were apparently unaffected by bleaching as no significant D.P. changes were produced by the hypochlorite.

The sulfur and "carboxyl" content of the pulps were functions of the severity of bleaching, both progressively decreasing as the bleach-

ing conditions were made more severe. Carboxyl content of the A.R.C. fraction isolated from the pulp increased under these conditions. Microscopic examination of the Klason lignin residues obtained from all the pulps revealed a wealth of structural detail. Staining techniques were used to determine the location of lignin and sulfonic acid groups in the pulp. While the sensitivity of the methods are not as great as might be desired, they indicated that most of the lignin and sulfonic acid groups present in the bleached and unbleached pulps were present in the "middle lamella" region of the shives.

Significant changes in pulp physical properties were produced by the action of hypochlorite. Filtration resistance, a measure of pulp drainage characteristics, was a function of the amount of hypochlorite applied in the bleaching stage. Specific surface, compressibility, and effective specific volume, which are related to filtration resistance by theoretical considerations, were also increased by bleaching. Sheet density appeared to be a key factor in the relationship between the strength of handsheets prepared from beaten, bleached pulps, and the amount of hypochlorite applied in the stage. When sheet density was plotted as a function of beating time for all of the bleached pulps, a family of curves with the per cent hypochlorite applied in the bleaching stage as a parameter was formed. Tensile strength was plotted as a function of sheet density for both bleached and beaten pulps. All points fell on approximately the same line, whether that sheet density was reached by bleaching or beating.

These observed effects can be unified by the hypothesis that delig-

nification is responsible for them. Other hypotheses can explain individual effects, but none unifies the chemical and physical effects. The most interesting chemical change, the decrease in "carboxyl", really represents a decrease in ion-exchange capacity of the pulp. Staining techniques indicate that lignin contains sulfonic acid groups which would be expected from theoretical considerations. Delignification should therefore decrease the sulfur content of the pulp. The sulfonic acid groups contribute to the over-all ion exchange capacity of the pulp, and if they are removed faster than the carbohydrates are oxidized, the apparent carboxyl content of the pulp should decrease. This conjecture is verified by the experimental data.

Physical properties are affected in a predictable manner by delignification. Changes in specific surface can be partially explained by the disintegration of shives into individual fibers. Destruction of shives should also increase compressibility. The presence of lignin within individual fibers has an effect on the swelling of fibers in water as it is present as a coherent nonswelling inelastic network. Removing parts of this lignin structure from the fiber by bleaching should then increase fiber swelling. This is in accord with the experimentally determined facts. As fiber swelling increases, there must be a concomitant increase in specific surface, another factor contributing to the increase in surface produced by bleaching.

The experimental data demonstrated that handsheets of a given density had a given strength, whether that density was reached by bleaching or beating. This relationship probably holds only for these

specific experimental conditions. It does not suggest that the fiber surfaces produced by bleaching or beating are identical; indeed, experimental data suggest this is not the case. It does suggest they are equivalent. An important factor in sheet density is the number of carbohydrate-carbohydrate bonds. Beating increases the number of these bonds by mechanically increasing the fiber surface. Bleaching increases the number of these bonds by removing lignin which exposes the underlying carbohydrate surfaces and indirectly increases surface area.

Bleaching conditions were not severe enough to degrade the fiber to such an extent that D.P. was a controlling factor in sheet strength. If this point had been reached, the "equivalence" of bleaching and beating in strength development would certainly break down.

In conclusion, it would seem that the important chemical and physical effects but not the brightness increase, produced by hypochlorite bleaching can be explained by the delignification of the pulp.

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2. Quick, R. H. A study of the order and nature of aspenwood hemicelluloses removed during a neutral sulfite semichemical cook. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1955. 82 p.

3. Boehm, R. H. A study of the effects of chlorination and extraction on carbohydrate fraction of an aspen neutral sulfite semichemical pulp. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1955. 84 p.

4. Bjorkqvist, K., Gustafsson, S., and Jorgensen, L., Svensk Papperstidn. 56, no. 19:734-8 (Oct., 1953).

The bleaching of NSSC birch and sulfite pulps by chlorination-extraction and chlorination-extraction-hypochlorite sequences was investigated. Pulps were analyzed for pentosans, uronic acid, and lignin. It was found that the pentosans and uronic acids were resistant to bleaching as long as the pH was between 8.5 and 10. Carbohydrate analysis was carried out by hydrolyzing the pulps and chromatographing the resulting sugars. Results show that non-cellulosic hexosans are completely removed by bleaching. Losses in bleaching birch NSSC, expressed as per cent of amount originally present in the wood:

	Chlorine			Hypochlorite		
Chlorine treatment, %	6	12	24	6	12	24
Total losses	27	31	38	33	35	38.5
Pentosans	21	21	23	22	22	25
Noncellulosichexosan	67	76	100	95	100	100
Uronic acid	56	58	60	72	92	99
Lignin	62	78	95	72	92	99

5. Haywood, G., Paper Trade J. 138, no. 53:28, 30, 32 (Dec. 31, 1954). Bleaching conditions for single-stage hypochlorite and CEH stages are given, and the effect of these two bleaching operations on the properties of NSSC poplar, gum, oak, hickory, and maple are presented. It is stated that high consistency (10%) in the extraction and hypochlorite stages results in a cleaner pulp with slightly less strength than low consistency (2.5%) operation of these stages.

6. Parsons, S., and Lausman, H. J., Tappi 34, no. 3:97-102 (March, 1951). The bleaching of NSSC pulp by single-stage calcium hypochlorite, single-stage sodium peroxide, and chlorination-extraction-hypochlorite sequences was investigated. Effect of alkalinity on hypochlorite was studied. Results indicate the pH 9 at end of stage is a satisfactory operating condition. Single-stage bleaching can produce brightness of about 75 G.E., multistage can produce brightness of 80-82 G.E. and the pulp has less reversion than the single-stage bleach.

7. Simmonds, F. A., and Kingsbury, R. M., Paper Trade J. 124, no. 4:53-60 (Jan. 23, 1947).

Results on the bleaching of NSSC hardwoods are presented. Depending on the type of wood, lignin content of the pulp, and the desired brightness, chlorine consumption may run from 10-30% of the pulp weight. For low brightness (75 G. E.) and small increases in strength, single-stage hypochlorite or peroxide bleaching is satisfactory; yield, is about 98% of the unbleached pulp. Multistage bleaching gives greater strength increases, brightness of 80$\pm$, and a yield of 80% based on unbleached pulp.

8. Chidester, G. H., Paper Trade J. 129, no. 20:84-9 (Nov. 17, 1949).

A general discussion of the effect of cooking and bleaching variables on pulp quality is presented.

9. Trivedi, S. A., Kingsbury, R. M., and Simmonds, F. A., Paper Ind. 29, no. 10:1443-53 (Jan., 1948).

Strength properties of aspen NSSC pulps given different types of treatments are compared. Pentosans, alpha, beta-cellulose and lignin determinations are presented. Typical strength data is presented below:

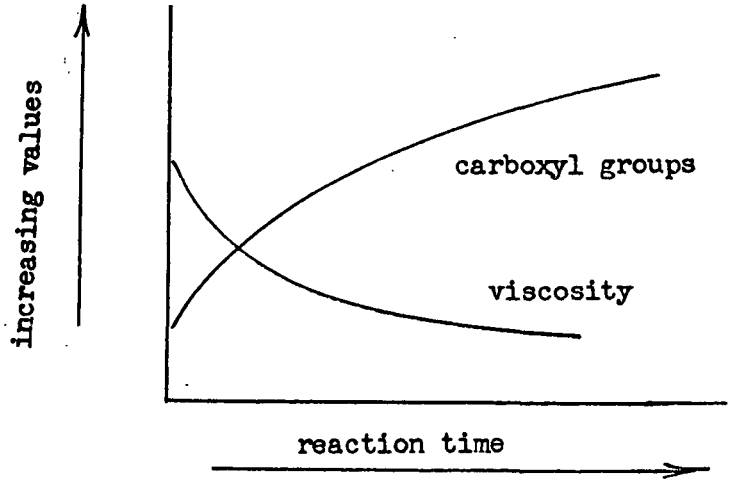
	Freeness,	S.R.	Burst	Tear	Tensile	G.E.
No treatment (u.b. pulp)	710	0.57	0.95	20.3		
Chlorination (12%, u.b. pulp basis)	650	0.70	1.10	24.0		
Extraction (0.9% NaOH, u.b. basis)	555	0.94	1.10	29.2		
NaOCl (3.2%, u.b. pulp basis)	535	1.08	1.01	33.0	81.5	
Extraction (3.5% NaOH, u.b. basis)	715	0.58	1.15	19.8		
NaOCl (3.0% u.b. pulp basis)	520	1.02	1.02	34.0	82.0	

10. Lekander, K., and Stockman, L., Svensk Papperstidn. 58, no. 21:755-85 (Nov., 1955).

The authors studied the influence of pH, temperature, and pulp consistency on the properties of a sulfite pulp bleached with hypochlorite (as the last stage of a bleaching sequence). They found that brightness, pulp viscosity, alpha-cellulose and carboxyl all increased as the pH of the bleaching stage was increased from pH 7 to 11. At the same time, beta-cellulose, copper number and yellowing decreased. The effect of temperature on the course of the reaction is negligible, but the rate increases with increasing temperature, doubling for every 7°C. rise. Pulp consistency is important only as far as brightness development is concerned; brightness decreases as consistency increases.

11. Sihtola, H., and Gustafsson, G. R., Paper and Timber (Finland) 32, no. 10:295-305 (1950).

The authors investigated the oxidation of pulp by hypochlorite extensively overbleaching to enhance the changes. The course of the reaction was followed by carboxyl content, copper number, brightness, alpha-cellulose and pulp viscosity. The general shape of the curves is indicated in the graph:



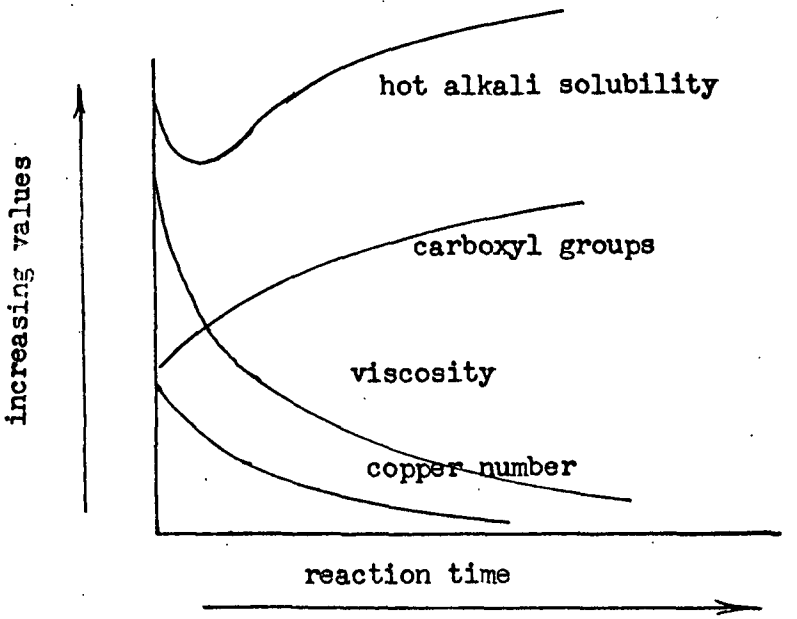
at 3.1%.

12. Gustafsson, G. R., Paper and Timber (Finland) 31, no. 17:308-9 (1949).

Hypochlorite oxidation was studied as a function of pH, and the extent of oxidation followed by copper number and carboxyl determinations. The rate of oxidation was very dependent on pH, in the same manner as cellulose.

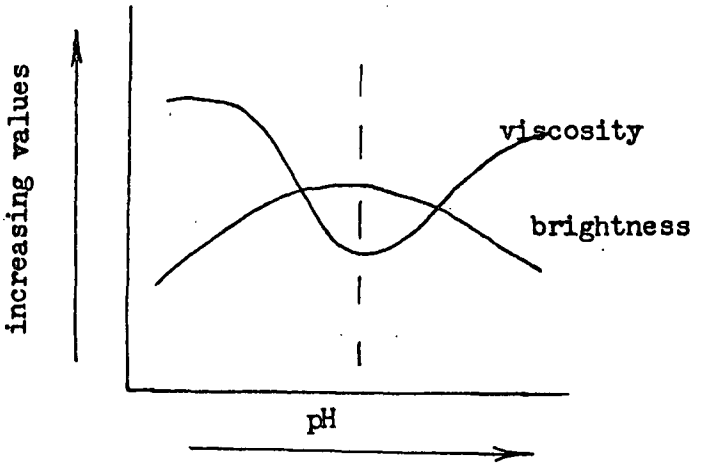
13. Samuelson, O., and Ramsel, K., Svensk Papperstidn. 53, no. 6:155-63 (March 31, 1950).

The authors bleached pulp at pH 10 with 2% active chlorine and measured changes in pulp properties with time. The results are presented in the graph to indicate the trends that were found:



14. Rapson, W. H., Paper presented at Fundamentals of Bleaching Conference, The Institute of Paper Chemistry, Sept. 15, 1955: Tappi 39, no. 5:284-95 (May, 1956).

A series of bleaches was carried out in buffered hypochlorite solutions: in the neutral range, alkali solubility of the pulps is high due to the formation of aldehyde and keto groups which are oxidized to carboxyl at higher pH. It was found that the hot alkali solubility correlated with color stability. No relation between oxidation potential and measured quantities was found.



15. Heidt, L. J., Gladding, E. K., and Purves, C. B., Paper Trade J. 121, no. 9:35-43 (Aug. 30, 1945).

The authors give theoretical reasons why certain oxidizing agents

can produce dialdehyde oxycelluloses and others cannot. The critical factors are: molecular size, the next lower valence state of the oxidant must be 2, rather than 1 or 3 lower than the original state, and the molecule must coordinate at least 2 more hydroxyl groups than it normally does. Experiments show the validity of these criteria. Hypochlorite is shown to be incapable of producing the dialdehyde type of oxycellulose.

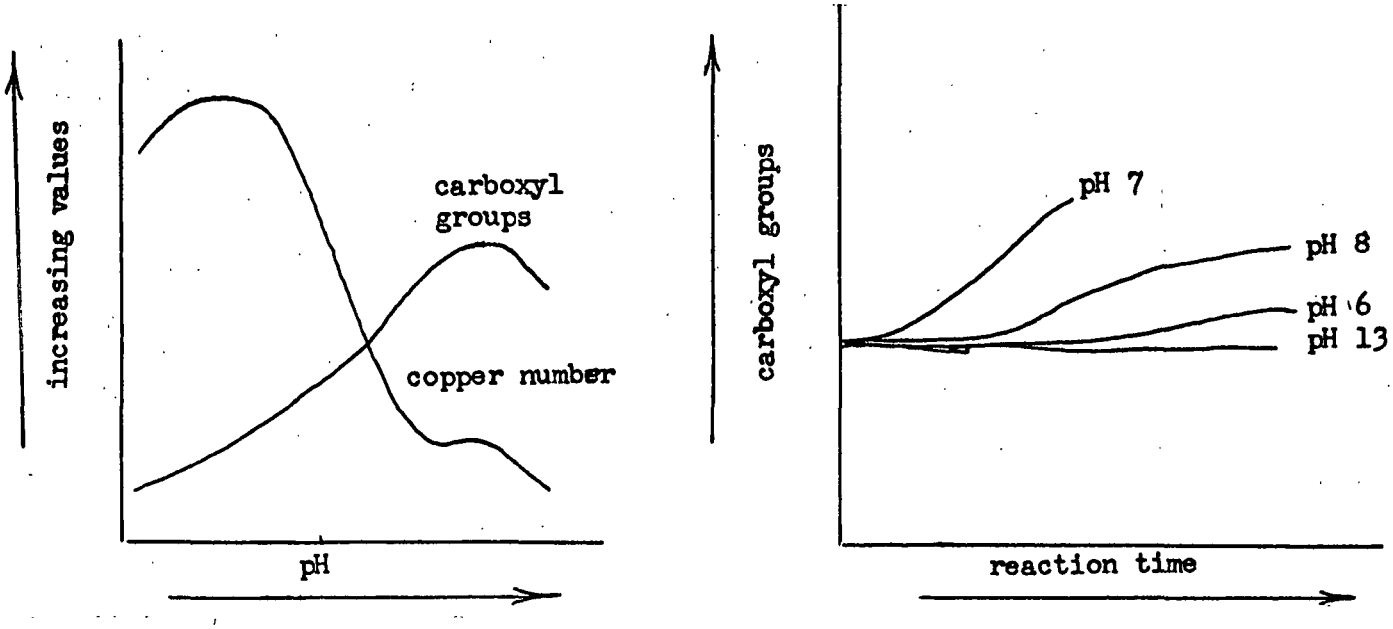
16. Carmody, W. R., and Mears, J. S., Paper Trade J. 106, no. 20:38-40 (May 19, 1938).

The authors considered the rate of the oxidation reaction to be proportional to the hypochlorite concentration and the concentration of oxidizable groups. Approximate equivalence of these groups and the bleaching agent would make the rate proportional to the square of the hypochlorite concentration. They believe that the initial fast reaction is substitution, which is then followed by the slower oxidation step.

17. Jayme G., and von Köppen, A., Das Papier 4:373-8, 415-20, 455-62 (Oct., Nov., Dec., 1950)

18. Birtwell, C., Clibbens, D. A., and Ridge, B. P., J. Textile Inst. 16:T13-51(1925).

Cotton fibers were oxidized with 29% chlorine as hypochlorite, on the basis of the fiber. The reaction was carried out at 25°C. and 1% consistency. Results of the investigation are shown in the two graphs:



19. Helfrich, B., and Lutzmann, H., Ann. 541:1-16 (1939).

The authors showed that alkaline cleavage will result spontaneously if an ether link is β to a strong electronegative group and the carbon atom has a free hydrogen atom. The inductive effect of the electronegative group makes the hydrogen acidic enough to be removed by a strong base. The resulting electron shift splits the molecule between the ether oxygen and the β carbon atom:

$$R\text{-}O\overset{H}{C}CCHO + B \rightleftharpoons [-ROC\ddot{C}CHO]^- + BH^+$$

$$[R\text{-}O\text{-}C\ddot{C} - CHO]^- \longrightarrow [RO:]^- + [C{=}CCHO]$$

$$[RO:]^- + BH^+ \longrightarrow ROH + B$$

20. McBurney, L. F. Oxidative degradation. In Ott, E., and Spurlin, H. M. Cellulose and cellulose derivaties. 2nd edition, Vol. I. p. 147-53, New York, Interscience, 1954.

21. Kaverzneva, E. D. The transformations occurring during oxidation of cellulose. Communication from the XIII International Congress of Pure and Applied Chemistry, Stockholm, 1953. (Translation).

The author studied the chemical properties of cellulose oxidized

with different oxidants. Evidence for the presence of certain functional groups is presented. The presence of hydroxyketo groups was shown by converting them to the enediol form in strong acid or alkali and testing for the enediol with arsenophosphotungstic acid. Reduction of ketones with hydroxylamine was also carried out. Differences in the total carboxyl content and that determined by decarboxylation with HCl were attributed to the presence of lactones. The presence and amount of carbonic acid ester was determined. A compilation of pertinent data is presented:

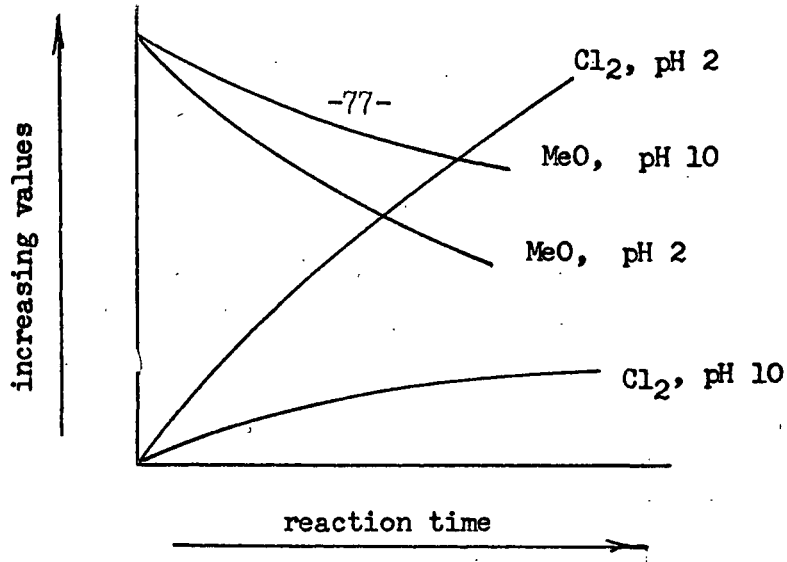
Sodium Hypochlorite Oxidation

Condition of Oxidation	Carboxyl/100 Glucose Residues		Carbonic Acid Ester
	Total	Decarboxylation	
Acid	0.42	0.76	0.16
Neutral	0.61	0.83	0.06
Alkaline	1.44	0.83	0.02

The amount of carbonate ester formed is not enough to account for the alkali sensitivity of bleached pulps.

22. White, E. V., Swartz, J. N., Peniston, Q. P., Schwartz, H., McCarthy, J. L., and Hibbert, H., Tech. Assoc. Papers 24:179-89(1941).

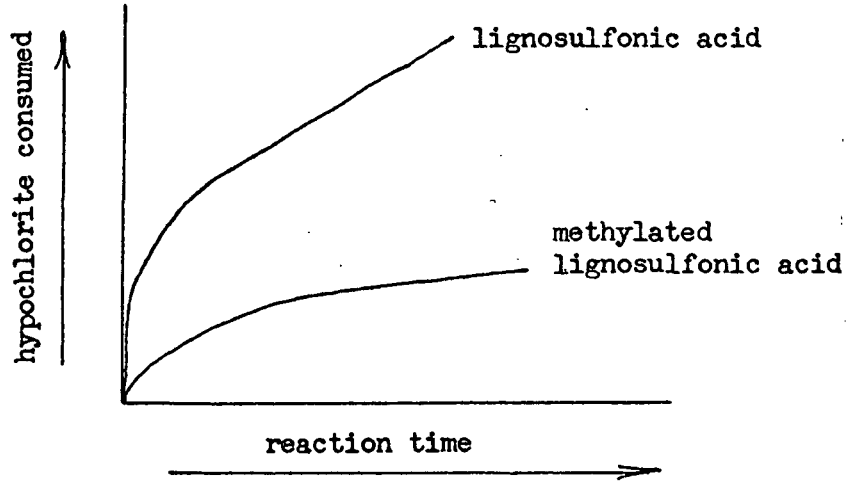
The authors, investigating the bleaching reactions, show that lignin is chlorinated even at high pH where oxidation is predominant. Methoxyl content decreases at all pH ranges as the oxidation of the lignin proceeds.



A proposed mechanism has been set forth to fit these facts.

23. Richtzenhain, H., and Alfredsson, B., Acta Chem. Scand. 7, no.8: 1177-85(1953).

Experimenting with model compounds, the authors concluded that appreciable consumption of hypochlorite does not take place unless the position ortho or para from a phenolic hydroxyl in the aromatic nucleus is unsubstituted. If the phenolic hydroxyl is masked by ether linkage, reaction with hypochlorite is very slow unless a readily oxidizable side chain is present. The first 6-7 moles of hypochlorite were assumed to react by chlorination, as no change in the ultraviolet absorption spectrum takes place.



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APPENDIX

EXPERIMENTAL PROCEDURES

CHIP PREPARATION

The wood used in the experimental program was obtained in northern Wisconsin near Rhinelander. Two aspen trees were felled April 14, 1953 and cut into 4-foot lengths. The trees were 23 and 29 years old, and had 8 and 9 rings per inch, respectively.

Chips were prepared from the peeled aspen logs in the Institute 2-knife, 36-inch Carthage chipper set to cut a 3/4-inch chip. The chips were screened and those passing a 1 by 2-inch screen and retained by a 1/4-inch screen were collected for the subsequent cooks. Moisture samples were taken after screening, and the green chips were then stored in glassine-lined kraft bags. The chips were cooked within a month after preparation.

EXPERIMENTAL PULPING

Several cooks were made in Pulping Laboratory digester No. 4 (8 kilo chip capacity, equipped with external heat exchanger and circulation) to establish conditions that would produce easy bleaching pulps. To determine the proper chlorine distribution for the bleaching stages, a series of CEH bleaches at different levels of total available chlorine and distribution of chlorine between the chlorination and hypochlorite stages were carried out. The results of these experiments are presented in Figure 13.

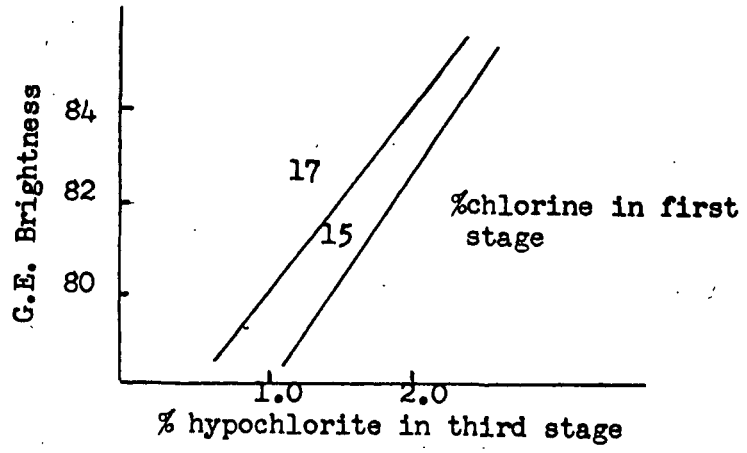


Figure 13

The cooking conditions selected for the experimental work are tabulated in Table XIII.

TABLE XIII

COOKING CONDITIONS FOR EXPERIMENTAL PULPS

Time, min.	Temp., °C.	Cooking Liquor Data	
30	100	Water ratio	5:1
45	120	Sodium sulfite,[1] %	18
60	125	Sodium carbonate,[1] %	5
90	125	Cooking liquor pH	11.5
105	145	Spent liquor pH	7.5
120	165	Yield, %	75.3
270	165		

[1]Ovendry wood basis

Following this schedule, a large cook (54 kilo of chips) was prepared in the A. O. Smith tumbling digester. The pulp from this cook was used in the investigations which were carried out in the

summer months. Changes in bleach demand on storage made it necessary to prepare another cook in the tumbling digester, and all conditions were identical, except that this cook was maintained at maximum temperature 20 minutes longer. This cook had a yield of 70% and a permanganate number of 44.5.

The pulp was blown into a blow tank at the conclusion of a cook. The chips were collected as soon as possible and refined while still hot in the Institute Bauer refiner, with plates set at zero clearance to give a fairly well refined stock with a minimum of shives.

The refined pulp was placed in a stainless steel wash tank and given three separate washes with tap water to remove most of the chemical retained by the fibers, screened through two flat screens with 0.010-in. slots, and collected on muslin-covered wash boxes. Excess water was removed from the screened pulp by centrifuging. The pulp was then passed through the laboratory pulp shredder several times to break up large lumps and randomize the pulp. All screened pulp was sampled for moisture content at this time, then stored in pliofilm bags at 5°C. with 0.1% formaldehyde added to prevent bacterial decay. The method proved satisfactory as the chlorine demand of this pulp did not change on storage.

EXPERIMENTAL BLEACHING

The bleaching of the screened pulp will be considered in two steps, first the chlorination and extraction stages, and then the hypochlorite stage.

Chlorination and Extraction

The screened pulp was chlorinated with gaseous chlorine in the Pulping Laboratory chlorinator at 3% consistency. Temperature was that of the city water supply, varying between 14 and 24°C. The reaction was allowed to proceed to the exhaustion of the chlorine as indicated by the starch-iodide paper test. Twelve per cent chlorine (ovendry unbleached pulp basis) was added in all chlorinations.

After chlorination the pulp was washed on a muslin-covered wash box, first with cold and then with hot filtered tap water. Progress of the washing could be observed by the color of the pulp. When the pulp turned purple, the wash water pH was about 5-6 (pH test paper) and the washing was then stopped. The pulp was dewatered and ready for the caustic-extraction stage.

Caustic extraction was done at 10% consistency, 40°C., with 2% sodium hydroxide on the basis of the unbleached pulp, for 1 hour. The reaction was carried out in a jacketed kettle to maintain proper temperature control; stirring was done periodically with a rubber glove. When the extraction was completed, the pulp was then dumped from the kettle onto a muslin-covered wash box to permit most of the liquor to drain off, followed by a short wash with hot tap water, then soaked in three changes of water in a stainless steel wash tank. This procedure removed most of the degraded and solubilized products created by the chlorination and extraction stages and permitted blending of several different pulp batches minimizing the effects of slight variations in the chlorination stage.

The extracted pulp was centrifuged to a final consistency of ca. 25%, the cake from the centrifuge broken up in the pulp shredder, then several extractions blended by passing them simultaneously through the shredder. This gave a pulp of uniform hypochlorite consumption for the hypochlorite stage, minimizing the variations introduced in duplicating the chlorination and extraction stages.

At this point, difficulties arising from the storage of the pulp from the extraction stage were encountered. Initially, a large "master batch" of extracted pulp had been prepared and stored at 25% consistency with formaldehyde added to prevent bacterial attack (the same technique used in storing the unbleached pulp), but it was found that the hypochlorite demand of the pulp changed radically on storage. This difficulty was later identified as probably a diffusional effect, but created a host of problems until it was overcome by the simple expedient of solvent-exchange drying.

TABLE XIV

PULP YIELDS, UNBLEACHED PULP BASIS

Stage	Yield, %
Chlorination	84.3
Extraction	80.5

Hypochlorite Stage

Bleach liquor for this stage was prepared by bubbling chlorine gas into a solution of reagent-grade sodium hydroxide; the liquor then tested according to Institute Method 112. Blended pulp directly from

the extraction stage was bleached with sodium hypochlorite under the following conditions:

(1) Pulp consistency: 10% (ovendry pulp basis)

(2) Temperature: 40 ± 1°C.

(3) pH maintained between 10.0 and 10.5 during reaction by addition of sodium hydroxide

(4) Reaction mixture stirred with rubber glove to insure complete mixing

(5) Hypochlorite concentration expressed as per cent available chlorine on the basis of the bonedry pulp charged to the stage

The pulp was mixed with 40°C. water to obtain bleaching consistency, and the slurry allowed to equilibrate in the water bath until the temperature was 40 ± 1°C., the bleach liquor then added to the pulp, and the mixture stirred by hand with a rubber glove for 5 minutes initially, and every 20 minutes thereafter to insure uniform bleaching.

Bleaching was stopped by sucking off as much as possible of the bleach liquor on a Buchner funnel, then immediately transferring the pulp to a wash box and washing it with hot filtered tap water. Brightness sheets were taken at the onset of the washing period. After washing for 1/2 hour, the pulp was placed in a large stoneware crock and soaked in hot water for 4 hours. It was then returned to the wash box and washed for another 20 minutes to completely wash out soluble reaction products. For liquor studies on the 1.5 and 6 pulps, the reaction was stopped by sodium sulfite. Determination of residual chlorine in the spent liquors presented some difficulties at the higher hypochlorite concentrations as the unconsumed hypochlorite

reacted with organic materials in the liquor at a rapid rate. This accounts for the differences observed in the chlorine consumption data. The magnitude of the change is shown in Figure 14.

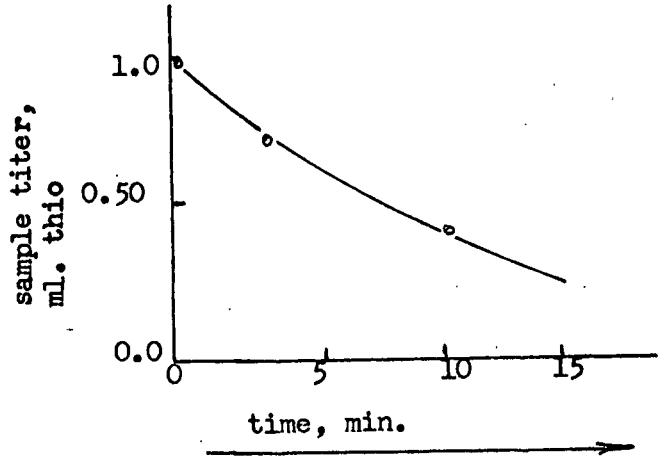
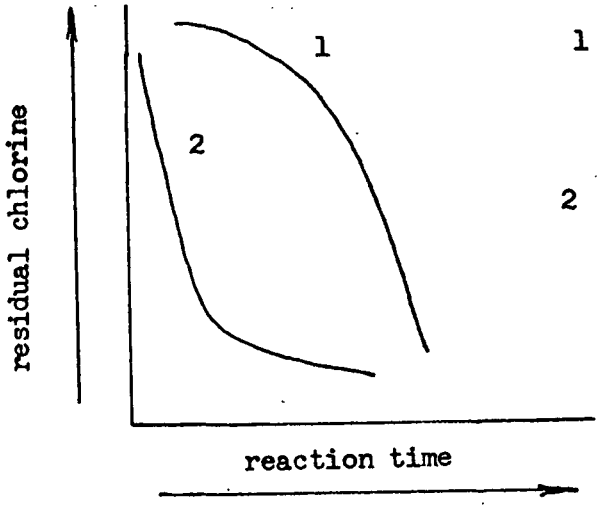


Figure 14

BLEACH DEMAND CHANGES ON STORAGE

In the initial phases of investigation a master "batch" of chlorinated and extracted pulp was prepared and stored in the Cold Room. The intent was to draw pulp from this batch for the hypochlorite experiments, eliminating the necessity for a chlorination and extraction before each experiment. It was felt that use of a "master batch" would eliminate the small variations that inevitably arise in a series of chlorination and extraction stages.

The hypochlorite consumption of the "master batch" changed very markedly on storage, making duplication of results impossible. The effect on chlorine consumption as a function of bleaching time is indicated in a general way in Figure 15.



1 Bleached immediately after extraction or solvent dried pulp

2 Pulp stored at 25% consistency for 4 days

Figure 15

This effect was not discovered until a month after the bleaching experiments were started, when it was felt necessary to recheck some work. Several tests were made to characterize the change more fully and determine if the initial bleach demand of the pulp could be restored. Mild acid extraction (pH 5.1, temperature 25°C., 1.5 hours extraction) brightened the pulp; mild alkaline extraction (pH 11.7, temperature 26°C., time 1.5 hours) darkened the pulp; neither treatment affected the bleach demand. Bleaching with 2% hypochlorite, which normally increased the brightness to 80, decreased the brightness to about 53. Solvent drying stopped the change in bleach demand. Color changes produced in the pulp by acid and alkaline treatments show the indicator effect of the colored components which are similar to those reported for kraft pulp (48). Darkening of the pulp by the addition

of what was normally the amount of hypochlorite required to produce bleaching parallels the behavior of spruce sulfite pulp when it is treated with 10-20% of its bleach demand (49). These facts, coupled with the fact that solvent drying arrests the change, point to a diffusion of hypochlorite-consuming materials from the inner parts of the fiber structure to the surface, where they are immediately available to the hypochlorite.

SOLVENT DRYING

"Solvent drying" as used in this work is the displacement of water from the pulp by alcohol, followed by subsequent air drying. Three effects are produced: (1) Most of the water is removed from the pulp; (2) about half of the material soluble in hot 95% ethanol is removed by the alcohol that is used to displace the water; (3) the fiber structure does not collapse nearly as much as in air drying (no hornification), making the pulp a great deal easier to disperse in water than air-dried pulp. Initially, the pulps to be chemically tested were air dried in a Freas oven at 30°C. They exhibited extreme hornification; complete dispersion in water was impossible, even after prolonged soaking. Klason lignin could not be determined until the pulps were ground to pass a 40-mesh screen in a Wiley mill. Photometric determination of lignin by the 85% phosphoric acid method was erratic. Difficulties were also encountered in the hemicellulose determination. These difficulties probably all had their common source--the high hemicellulose content of the pulp bonded the fibers, either to each other or internally, to the point where extreme treatment, outside the range of normal procedures

would have been necessary to completely redisperse the pulp. All of these difficulties were eliminated with solvent drying.

TABLE XV

COMPARISON OF SOLVENT DRIED AND NEVER DRIED PULPS AFTER CHLORINATION AND EXTRACTION STAGE

Property	Never Dried (25% Consistency)	Solvent Dried
Carboxyl, meq./100 g. pulp[1]	14	14
Copper number	0.2	0.2
95% ethanol extract, %	0.7	0.4
Moisture content, %	75	10

[1]Determined using ordinary distilled water

The determination of filtration resistance, and the derived values of specific surface and effective specific volume, required special pulp preparation. The solvent-dried pulps could not be used as no particular pains were taken in washing the pulps to keep conditions exactly constant, nor was the solvent drying step completely standardized. These refinements were not necessary for satisfactory chemical analysis and handsheet preparation. However, filtration resistance is extremely sensitive to the past history of the pulp; different amounts of washing cause slight differences in the amounts of fines in the pulp, and differences in solvent drying have a small effect on the "hornification" that takes place. These variables caused erratic results in the filtration resistance determination on the pulps. Rather than attempt to standardize the washing and solvent drying steps, a new series of pulps (series II) were prepared in identical fashion to series I (solvent dried), but the bleaching stopped by the addition of sodium sulfite and carefully dewatered on a Buchner funnel. These pulps were never washed

or dried, but were stored at 5°C. and 10-15% consistency in pliofilm bags until the filtration experiments could be carried out.

SPECIAL EASY BLEACHING PULP

Before the role of diffusion in changing the bleach demand was clearly understood, a chlorinated and extracted pulp was prepared in such a manner as to minimize any possible reactions that might occur. The very easy bleaching properties of this pulp make it of at least passing interest. Probably the extended soaking period after the caustic-extraction stage during which the acidification was carried out is primarily responsible, though the sodium sulfite treatment is in effect an additional extraction step. The steps in the preparation of this pulp were:

(1) Chlorination, carried out in the usual fashion

(2) 2% sodium sulfite added at the end of the chlorination as an antichlor; the pulp was stirred 10 min. after the addition of the sodium sulfite

(3) Caustic extraction, carried out in the normal manner

(4) Pulp placed in a 22-liter crock filled with filtered tap water; the pH was adjusted to 6.1 with acetic acid, the acid being added over a period of 24 hours to insure equilibrium.

The behavior of this pulp on bleaching is compared in Table XVI with that of one made under normal conditions.

TABLE XVI

COMPARISON OF BLEACHING BEHAVIOR OF PULPS

Bleaching Time, min.	G.E. Brightness, %		Chlorine Consumed, %	
	Normal	Special	Normal	Special
0	68.5	72.6	—	—
3	72.1	--	--	--
13	72.9	82.6	10.7	1.4
30	—	86.0	--	--
53	78.0	--	--	--
60	—	86.4	--	11.2
120	80.0	85.5	80.0[1]	13.5

[1]Estimated from plotted data

The special pulp was solvent dried from methanol before bleaching.

ANALYTICAL PROCEDURES

ASH

Ash determinations were made by carefully charring the material in a crucible, stopping the combustion before all the organic matter was burned off. Two drops of sulfuric acid were added to the crucible to convert all inorganic salts to sulfates, after which the acid was carefully fumed off on a hot plate. When the evolution of sulfur trioxide ceased, the crucible was ignited to constant weight in a muffle furnace at 600°C., then cooled in a desiccator and weighed. The results were calculated as sulfated ash. The sulfated ash sample was dissolved in distilled water, filtered through S&S 589 filter paper and the residue on the paper washed until the filtrate contained no sulfate ion. The paper was returned to the crucible, ignited on a hot plate to burn off the paper without danger of actual flaming, and then ignited to constant weight at 600°C. The residue was calculated as insoluble ash. The corrected ash for the hemicellulose determination ash correction was calculated by the equation (2):

$$\text{corrected ash} = \frac{(\text{water-soluble ash})\ \frac{76}{174} + \text{insoluble ash}}{\text{sample weight of ovendry hemicellulose}} \qquad (2)$$

OVENDRY CONTENT

Duplicate samples were dried in an oven at 105°C. for 16 hr. or until constant weight was reached. In the case of pulp or A.R.C. samples that had been dried from solvents, the solvent was displaced from the pulp by adding distilled water to the sample before placing it in the oven.

KLASON LIGNIN

Lignin was determined on the pulp samples by Institute Method 428 (1951). Soluble lignin was determined on the filtrate by the measurement of the absorption of the solution at 230 mu. The equation relating the lignin content of the solution and absorption is:

Lignin, g./l. = Absorbance/ (cell width, cm.) (absorptivity)

The value of the absorptivity is 42 at 230 mu. and 15 at 280 mu., according to Buchanan, Brauns, and Leaf data (26) on the ultraviolet absorption of native lignin.

EXTRACTIVES

The pulp was extracted with 95% ethanol according to Institute Method 428. Actual weight of the extractives was determined by evaporating off the alcohol and drying to constant weight in a 50°C. vacuum oven.

DETERMINATION OF VISCOSITY AND D.P.

HEMICELLULOSES

A weighed sample of hemicellulose, corrected for ash and moisture, was suspended in 10 ml. of distilled water. After 10 minutes, 15 ml. of a concentrated potassium hydroxide solution was added to produce 25 ml. of solution containing 10% potassium hydroxide. The solution was put on a shaker for 1 hour before viscosity determinations were attempted. Samples were filtered through a medium-porosity fritted-glass micro-

funnel directly into the viscometer; this step removed a minute amount of small particles that interfered with the viscosity measurements. The funnel was calibrated to contain the correct volume for the viscometer, then always filled to the calibration mark to insure that all measurements were made with the same liquid head in the viscometer. The D.P. of the hemicelluloses was determined by measuring the viscosity of various concentrations of hemicellulose, calculating the (specific viscosity/concentration) values and plotting them against concentration. The intercept of the plot is the intrinsic viscosity, and is related to D.P.; by the following equation (49):

$$\text{D.P.} = (\text{intrinsic viscosity}) \,/\, 4.4 \times 10^{-3}$$

The constant was determined for aspen hemicellulose by osmotic pressure measurements by Thompson (49).

PULP AND A.R.C.

Pulp and A.R.C. viscosity was determined in 0.5 M cuen. Both materials were impossible to dissolve directly in the solvent so a 2-stage addition of 1.0 M cuen was employed. One-third of the required amount of cuen was added to the pulp (which was presoaked in the necessary amount of distilled water to give a 0.5 M concentration when all of the reagent was added) and the mixture shaken 1 hour. Then the remaining 2/3 of the cuen was added, and the shaking continued an additional 2 hours. The addition of cuen was carried out under nitrogen with the apparatus described by Browning, et al., (50).

Shear rate has a large effect on the viscosity determination at the high values of D.P. found in the pulp samples, and to be strictly

comparable, all determinations must be carried out at identical rates of shear. To avoid misleading conclusions it was deemed more realistic to determine the viscosity of the pulp and A.R.C. fractions at a fixed concentration and compare viscosity changes with the control pulp than to determine D.P. values for the pulps by the technique used for the hemicelluloses. Viscosity values were determined at 0.25 g. of ovendry pulp per 100 ml. of 0.5 M cuen, and the intrinsic viscosity calculated from the Martin equation (29). The D.P. of the pulp and A.R.C. samples was calculated from the relationship:

D.P. = 170 (intrinsic viscosity).

The constant was determined by Newman, et al., (51) for cellulose.

PERMANGANATE NUMBER

The high lignin content of semichemical pulps makes it necessary to modify the usual permanganate number method. One gram of pulp was disintegrated in 800 ml. of distilled water in a Waring Blendor for 4 minutes. The pulp was then washed into a 3-liter beaker with 1500 ml. of distilled water and 75 ml. of 4N sulfuric acid added. The reaction was timed from the addition of 75 ml. of 0.10 N potassium permanganate and run under the usual conditions of time and temperature. At the end of the reaction, 35 ml. of 10% potassium iodide was added and the liberated iodine titrated with 0.1 N sodium thiosulfate.

HEMICELLULOSE AND ALKALI-RESISTANT CELLULOSE

Hemicelluloses were extracted from the pulps by the procedure of Wise, et al., (25) using successive extractions with 5 and 16% potassium

hydroxide. These concentrations were used as they make it possible to compare the present results with those of Quick (2) and Boehm (3). It has been shown that this procedure gives good hemicellulose yields and smaller amounts of inorganic salts in the products than higher concentrations of potassium hydroxide. Alkali-resistant cellulose is the insoluble portion of the pulp remaining after the 16% potassium hydroxide extraction.

SULFUR DETERMINATION

The sulfur in the pulps was determined by the combustion-iodometric technique (ASTM Standard E30-47). The pulp sample is burned at high temperature in a stream of oxygen, converting the sulfur to sulfur dioxide, which is measured by its ability to react with free iodine. The accuracy of the method is ± 0.2 meq. sulfur/100 g. of pulp.

CARBOXYL DETERMINATION

The "carboxyl" groups were determined by the method of Wilson (28) which involves converting all groups that can exchange cations for hydrogen into their free acid form, washing out any excess acid, and measuring the amount of hydrogen ions bound by the pulp by their ability to partially neutralize a known volume of 0.01 N sodium bicarbonate. Several changes were made in the original method to improve its accuracy for this work. First, the sample size was reduced from 2 g. to 1 g. because the pulps tested had twice the carboxyl content of any previously used, and it is essential that the final pH of the sodium bicarbonate solution be 7.0-7.5 if the reaction is to be complete. Two

acid treatments were used to be sure of complete ion-exchange in the initial treatment. The Institute distilled water contained enough cations to give spuriously low results when it was used in the washing stage. To eliminate difficulties from the source, distilled water with half the conductivity of the regular supply was prepared by distilling deionized water over permanganate, cooling the distillate in a block tin condenser, and storing the water in a polyethylene bottle.

The endpoint of the titration used to determine the amount of sodium bicarbonate left after the pulp had been allowed to react overnight was determined by a pH meter instead of the methyl red indicator recommended by Wilson.

Results on pulp samples showed a rather large deviation from average, amounting to ± 0.4 meq./100 g. pulp. The alkali-resistant cellulose carboxyl results were in better agreement, deviating ± 0.2 meq./100 g. pulp from the average.

WET COMBUSTION PROCEDURE

Organic matter was determined in the spent bleach liquor by wet combustion. The method is based on the fact that carbon atoms in organic compounds are readily oxidized to carbon dioxide by a mixture of potassium dichromate and concentrated sulfuric acid; the amount of dichromate consumed in the reaction is a measure of the amount of carbon present. Any carbon atom directly attached to an oxygen, or in an aromatic ring, is readily oxidized and only a few compounds such as acetic acid are resistant to oxidation (52); consequently a satisfactory measure of total organic matter in the liquor can be obtained.

A known volume of bleach liquor was evaporated to dryness *in vacuo* after converting all of the acidic material present to sodium salts. This step was necessary to remove the hexyl alcohol used as a defoamer in the initial concentration of the bleach liquor for chromatographic analysis. This dry powder was dissolved in 10 ml. of distilled water and a 1.00-ml. aliquot oxidized with 5 ml. of potassium dichromate of known normality, and 8 ml. of concentrated sulfuric acid. Conditions of oxidation were identical with Institute Method 425. The method was calibrated by oxidizing known amounts of sugar under identical conditions and determining the amount of potassium dichromate consumed per mg. of carbon.

SUGAR ANALYSIS

The simple sugar composition of the spent bleach liquor was determined after hydrolysis. As sodium sulfite had been used to destroy the excess hypochlorite at the end of the bleaching reaction, hydrolysis was carried out in such a manner as to eliminate sulfite ion which interferes with some chromatographic tests for phenols.

The original bleach liquor solutions were concentrated *in vacuo* at 25°C. to *ca* 10 ml. and a 5-ml. aliquot taken for hydrolysis. The solution was treated with 20% sulfuric acid until evolution of sulfur dioxide in the cold ceased, then heated to boiling and the treatment continued until no more sulfur dioxide could be detected in the vapors which indicated the elimination of sulfite ion. The solution was refluxed for three hours after the addition of 50 ml. of 3% sulfuric acid. The solution was neutralized to pH 6.0 with barium hydroxide and the precipitated

barium sulfate removed by filtration. Ion exchange through Amberlite IR-120 replaced the barium with hydrogen ion. This solution was re-concentrated in vacuo to 10-15 ml.; a drop of pyridose solution was added to prevent fermentation, and the solution stored at 5°C. until used for analysis.

As the quantitative sugar analysis requires an "internal calibration" for each determination, accurately weighed out quantities of xylose, arabinose, and galactose were dissolved in exactly 25 ml. of distilled water to make a "known" sugar solution. The unknown (the bleach liquor sample) and three different concentrations of the known solution were spotted on a 7 by 24-inch Whatman number one filter paper. The paper was placed in the 10-3-3 system for 48 hours, removed, dried, and then the top 2 inches below the starting line clipped off with a pair of scissors, which removed all the strongly acidic components. The paper was then placed in the 9-2-2 system for 12 hours, which gave excellent separation of the sugars present and eliminated interferences which were caused by a phenolic material if the papers were chromatographed with only the 10-3-3 solvent. A weakly acidic material, which interfered with the arabinose determination if only the 10-3-3 system was used, "ran ahead" of the sugars in the 9-2-2 stage and therefore caused no difficulties in the analysis.

The sugars were determined by the method of Pridham (53). In this procedure, the chromatogram is sprayed with p-anisidine hydrochloride and heated for 10 minutes at 130°F. to develop the colored spots. The intensity of the color is directly relative to the concentration of sugar,

so by eluting the spots with 95% methanol and determining the optical density of the solution, the amount of sugar can be quickly determined.

The color is unstable unless precautions are taken. Stannous chloride is added to the p-anisidine spray reagent, and also to the 95% methanol solution. The spots are clipped out of the paper with scissors, placed into test tubes and eluted with 3 ml. of 95% methanol solution. In the present work, three different concentrations of knowns and one unknown were present for each sugar. A "blank" with an area equal to that of a "spot" is also eluted with the methanol solution, and then the optical density of the unknown based on the blank as zero concentration is measured on a Beckman DU spectrophotometer. From the values of optical density of the knowns, a plot of optical density vs. sugar concentration for a particular sugar is prepared. If no errors have been made, the solutions follow Beer's law, and the plot is a straight line. The concentration of the sugar in question in the unknown is then read directly from the graph. Pentoses were determined at 540 mu, hexoses at 400 mu. The precision obtained on duplicate determinations is quite good at high concentration, but appears to fall off if the concentrations become too low. Results on duplicate samples are given in Table XVII.

TABLE XVII

SUGAR ANALYSIS RESULTS
(mg./ml. hydrolyzate)

Sugar	Xylose	Arabinose	Galactose
1.5% Liquor	3.34	0.63	0.83
	3.37	0.54	0.87
	--	0.68	--
6% Liquor	2.88	0.28	0.57
	2.95	0.30	0.64
	--	--	0.53

HANDSHEET TESTING

Pulps were refined in a Jokro mill as this enabled complete beater evaluations to be made with small amounts of pulp. Refining was carried out in accordance with the manufacturer's instructions, and all pulps were soaked in water for at least four hours before the refining was carried out. Handsheets were made from the pulp on a standard British sheet machine, then tested according to Institute standards (1951):

Test	Institute Method
Conditioning of sheets for physical tests	503
Basis weight	504
Caliper and density	508
Bursting strength	510
Tensile strength	511
Opacity	524

Only one deviation from these standard techniques was necessary. The high hemicellulose content of the handsheets made it very difficult to separate the sheets made from well-beaten pulp from the blotters unless the sheets were air dried on the couch blotter for at least 20 minutes and then carefully transferred to a new blotter before pressing.

FILTRATION RESISTANCE

Filtration resistance, specific surface, effective specific volume, and compressibility were determined by the methods described by Ingmanson (30). In essence, the pulp to be tested is slurried in water at low consistency and filtered through a wire screen. Pressure drop across the screen is determined as a function of time for constant rate filtration conditions. This permits calculation of the filtration resistance of the pulp. Calculations now in routine use for this work are based on a modification of the ones reported in the literature. As the first step, the filtration constant, B, is determined from:

$$B = \underline{A}^2 \rho g / \underline{QC} \eta$$

where $\underline{A}$ = area through which filtration occurs

ρ = density of water

g = gravitational constant

η = viscosity of water at the temperature of filtration

C = slurry consistency, g. fiber deposited/cu. cm. filtrate

Q = volume filtered

R, the filtration resistance, is computed from the data by choosing equal pressure increments from the time-pressure drop curve, reading off the time θ, and calculation R by the relationship:

$$\underline{R} = B \Delta P_f / \underline{\theta}$$

ΔP_f = pressure drop

θ = time

The specific surface, Sw, and effective specific volume v cannot be determined until the compressibility c had been determined. This value is obtained by static loading of the pulp pad with known loads and then determining the pad volume, giving compressibility in terms of cubic centimeters per gram, and might be thought of as a concentration term. Taking equal increments of compressibility off the compressibility vs. load plot, the corresponding pressures are determined. These values are transferred to the time-pressure drop plot and its slope at the corresponding ΔP_f values obtained. The values of Sw and v can now be determined from the rectified Kozeny-Carmen equation:

$$(C \, d\theta/d \, P_f)^{1/3} = (B/ \, kSw^2) \, ^{1/3} \, (1 - vC)$$

The left hand member of the equation is plotted against C; the result is a straight line with negative slope. In this plot, the intercept is equal to $(B/k \, Sw^2)^{1/3}$, and the slope is $(B/ K \, Sw^2)^{1/3} v$; k is the Kozeny constant, taken as 5.55 for pulp fibers.

FIBER CLASSIFICATION

The Clark classifier (33) was used to determine the fiber length distributions of the pulps and prepare fiber fractions for shive counts and physical testing.

SHIVE COUNT

In this study, a shive was defined as any bundle of two or more fibers. Counting was done with the aid of a microscope, and at least two hundred fibers counted for each determination.